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MODIFIED FORM OF GRUNEISEN'S THEORY*

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ABSTRACT

In the present paper a modified form of Gruneisen's theory of thermal expansion of isotropic crystals has been given by assuming that the different vibration frequencies of the crystal lattice are associated with different Gruneisen constants. It has been pointed out that, from the theoretical standpoint also, the frequencies should have different Gruneisen constants. This has been further corroborated by calculating the Gruneisen constants for some of the principal spectral lines of the cubic crystals of sodium chlorate and ammonium chloride from the available Raman Effect data.

Formulation of the Modified Theory

From quantum theoretical considerations we know that the mean energy E of an oscillator of frequency ν at temperature T is given by

$$E = kT \, \frac{h\nu/kT}{e^{h\nu/kT}-1} .$$

where k is Boltzmann's constant.

Now, the free energy F is given by the relation

$$F - T\left(\frac{\partial F}{\partial T}\right)_V = E.$$

$$\text{or} \qquad \frac{dF}{dT} - \frac{F}{T} = \frac{h\nu}{T} \cdot \frac{1}{e^{h\nu/kT}-1} .$$

Thus

$$F = kT \log\left(1 - e^{-h\nu/kT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In the case of a crystal, let us assume that it consists of N molecules. If the number of atoms in a molecule be p there are 3 Np degrees of freedom which, we may suppose, are divided into j discrete frequencies. The statistical weight of a frequency ν_j is represented by the symbol σ_j which means that 3 Np σ_j degrees of freedom correspond to this frequency. The free energy of a gm-molecule is then given by

$$F = \Phi_0 + 3pRT \sum_j \sigma_j \log\left(1 - e^{-h\nu_j/kT}\right) \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where Φ_0 is the potential energy per gm-molecule of the atoms when they are at rest in their equilibrium positions. The equation of state can now be easily obtained from the condition that the pressure P is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

V being the molecular volume. On differentiating and multiplying both sides of (2) by V we obtain

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$$\left(P+\frac{\partial\phi}{\partial V}\right)V=\sum_{j}\gamma_j\sigma_j E_j\ldots\ldots\ldots\ldots(4)$$

where $\gamma_j=-\frac{\partial \log \nu_j}{\partial \log V}$ is the Gruneisen constant pertaining to the frequency ν_j and E_j is the energy of oscillation corresponding to the same. This can be evaluated from the Einstein energy function and is equal to 3 pRT $\frac{h\nu/kT}{e^{h\nu/kT}-1}$ In the Einstein theory of specific heat only one frequency is assumed so that the right hand member of equation (4) reduces simply to γE, a form in which the law was first expressed by Gruneisen himself. In the Debye theory the same result is achieved by tacitly assuming without proof that γ_j is the same for all the vibration frequencies. E_j in that case, however, has to be evaluated from a Debye energy function.

The atoms in the case of a crystal lattice are assumed to be held in position through the agency of attractive and repulsive forces which they exert upon one another. In the equilibrium position these forces exactly balance one another. In order to account for the elastic properties of solids it is necessary to suppose that, with increase of the distance between two atoms, the repulsive force falls off much more rapidly than the attractive force. It is further supposed that the attractive and repulsive forces obey simple inverse power laws as regards the distance between them, and that, apart from a constant, the potential energy ϕ of two atoms separated by a distance r is given by

$$\phi=-\frac{a}{r^m}+\frac{b}{r^n}\ldots\ldots\ldots\ldots(5)$$

Gruneisen showed that the potential energy in such a case can be expressed in the form of the relation —

$$\phi=-\frac{A}{V^{n/3}}+\frac{B}{V^{m/3}}$$

$$\text{or}=-\frac{A}{V^x}+\frac{B}{V^y}\ldots\ldots\ldots\ldots(6)$$

where a, b, A, B appearing in these two equations are constants and $x=n/3$ and $y=m/3$. Following Gruneisen's notation, if we put $\left(\frac{\partial\phi}{\partial V}\right)V$ equal to G (V), the equation of state of a solid becomes

$$PV+G(V)=\Sigma_j\gamma_j\sigma_j E_j\ldots\ldots\ldots\ldots(7)$$

If the external pressure is zero this reduces to

$$G(V)=\Sigma_j\gamma_j\sigma_j E_j\ldots\ldots\ldots\ldots(8)$$

In order to obtain the law of thermal expansion we have to determine V as a function of E and thus of T. In order to do this, the left hand side of (8) can be developed as a series of increasing powers of $(V-V_0)=\triangle$, where V_0 is the volume at absolute zero and under zero external pressure. Thus

$$G(V)=G(V_0)+\triangle\cdot\frac{d}{dV_0}G(V_0)+\frac{\triangle^2}{2!}\cdot\frac{d^2}{dV_0^2}G(V_0)+\ldots\ldots\ldots\ldots(9)$$

We have, then, to consider G (V_0) and its differential co-efficients at $V=V_0$

$$\left.\begin{aligned} &G(V_0)=V_0\,\frac{d\Phi_0}{dV_0}\\ &\text{Therefore}\ \frac{d}{dV_0}\,G\,(V_0)=V_0\,\frac{d^2\Phi_0}{dV_0^2}+\frac{d\Phi_0}{dV_0}\\ &\text{and}\ \frac{d^2}{dV_0^2}G(V_0)=V_0\frac{d^3\Phi_0}{dV_0^3}+\frac{d^2\Phi_0}{dV_0^2} \end{aligned}\right\}\ \cdots\cdots\cdots\cdots\cdots(10)$$

The differential co-efficients of Φ_0 are as follows :—

$$\left.\begin{aligned} &\Phi_0=-\frac{A}{V_0^x}+\frac{B}{V_0^y}\\ &\frac{d\Phi_0}{dV_0}=\frac{x.A}{V_0^{x+1}}-\frac{y.B}{V_0^{y+1}}\\ &\frac{d^2\Phi_0}{dV_0^2}=-\frac{x.(x+1)A}{V_0^{x+2}}+\frac{y.(y+1).B}{V_0^{y+2}}\\ &\frac{d^3\Phi_0}{dV_0^3}=\frac{x(x+1).(x+2).A}{V_0^{x+3}}-\frac{y.(y+1).(y+2).B}{V_0^{y+3}} \end{aligned}\right\}\ \cdots\cdots\cdots\cdots\cdots(11)$$

These can be simplified from the consideration that at the absolute zero and under zero external pressure the atoms are completely at rest and are in equilibrium.

Thus $$\frac{d\Phi_0}{dV_0}=\frac{x\,A}{V_0^{x+1}}-\frac{yB}{V_0^{y+1}}=0$$

or $$yB=xAV_0^{y-x}\qquad\cdots\cdots\cdots\cdots\cdots(12)$$

Substituting this value in equations (11) we obtain

$$\left.\begin{aligned} &\frac{d\Phi_0}{dV_0}=0\\ &\frac{d^2\Phi_0}{dV_0^2}=x(y-x)\,\frac{A}{V_0^{x+2}}\\ &\frac{d^3\Phi_0}{dV_0^3}=-\frac{(y+x+3)}{V_0}.\ \frac{d^2\Phi_0}{dV_0^2} \end{aligned}\right\}\ \cdots\cdots\cdots\cdots\cdots(13)$$

Using these relations in (10) we have

$$\left.\begin{aligned} &G(V_0)=0\\ &\frac{d}{dV_0}\,G(V_0)=V_0\frac{d^2\Phi_0}{dV_0^2}\\ &\frac{d^2}{dV_0^2}G(V_0)=-(y+x+1)\,\frac{d^2\Phi_0}{dV_0^2} \end{aligned}\right\}\ \cdots\cdots\cdots\cdots\cdots(14)$$

Now, we evaluate $\frac{d^2\Phi_0}{dV_0^2}$ in terms of K_0, the compressibility of the crystal at absolute zero and under zero external pressure. We have

$$K_0=-\frac{1}{V_0}\left(\frac{\partial V_0}{\partial P}\right)_T$$

Let us consider an isothermal change at the absolute zero in which the volume is changed from V_0 to V by increasing the pressure from zero to δP. We have

$$\Phi=\Phi_0+\Delta.\ \frac{d\Phi_0}{dV_0}+\frac{\Delta^2}{2!}\cdot\ \frac{d^2\Phi_0}{dV_0^2}+\cdots\cdots\cdots$$

By equation (13) the second term on the right vanishes.
Hence

$$\Phi - \Phi_0 = \tfrac{1}{2}\Delta^2 \frac{d^2\Phi_0}{dV_0^2}$$

But $\Phi - \Phi_0$, the increase in the potential energy, is equal to the mean pressure, $\frac{1}{2}\,\delta P$, multiplied by the diminution of volume $(V_0 - V)$, that is,

$$\Phi - \Phi_0 = -\frac{\delta P}{2}\cdot\Delta$$

Further,
$$\Delta = \frac{\partial V_0}{\partial P}\,\delta P = -V_0 K_0 \delta P$$

Hence
$$V_0 \frac{d^2\Phi_0}{dV_0^2} = \frac{1}{K_0} \qquad \text{......................(15)}$$

Thus, using (15), equations (14) become

$$\left.\begin{aligned} &G(V_0) = 0 \\ &\frac{d}{dV_0}G(V_0) = \frac{1}{K_0} \\ &\frac{d^2}{dV_0^2}G(V_0) = -(y + x + 1)\,\frac{1}{V_0 K_0} \end{aligned}\right\} \qquad \text{......................(16)}$$

Substituting the values of G(V) in equation (9) and neglecting the powers of Δ higher than the second we have

$$\frac{\Delta}{K_0}\left[\,1 - \frac{m+n+3}{6}\cdot\frac{\Delta}{V_0}\right] = \sum_j \gamma_j \sigma_j E_j \text{......... ....(17)}$$

The second term in the brackets is usually small and can be neglected, so that on differentiating

$$\frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right) = \beta = \frac{K_0}{V_0}\sum_j \gamma_j\,\sigma_j\,\frac{\partial E_j}{\partial T} \qquad \text{......................(18)}$$

where β is the co-efficient of cubical expansion and $\sigma_j \frac{\partial E_j}{\partial T}$ is the contribution of the frequency ν_j to the specific heat. Equation (18) is Gruneisen's law in the most general form which can be employed for the evaluation of β in conjunction with any theory of lattice vibrations.

Gruneisen considered the Einstein theory of specific heat according to which there is only one frequency of vibration of a solid namely, that in which one of the atoms is displaced about its mean position and the others remain at rest in their equilibrium positions. Thus, under these circumstances, equations (17) and (18) reduce to the simple forms :—

$$\frac{\Delta}{K_0}\left[\,1 - \frac{m+n+3}{6}\cdot\frac{\Delta}{V_0}\,\right] = \gamma E \qquad \text{......................(19)}$$

and
$$\beta = \gamma K_0 \frac{\partial E}{\partial T} = \gamma K_0 C_v \qquad \text{......................(20)}$$

It follows immediately from equation (20) that for a given substance the co-efficient of expansion is proportional to the atomic heat at constant volume.

At higher temperatures the second term within the brackets of equation (19) has to be used so that, if we put $\triangle = K_0 \gamma E$ approximately, we get

$$\beta = \frac{K_0}{V_0} \cdot \frac{C_V}{\left[1 - \frac{m+n+3}{6} \cdot \frac{K_0 \gamma E}{V_0} \right]^2} \quad \text{..................(21)}$$

Only the correction quantity in the brackets of the denominator depends on the law of force assumed in (5). Equation (21) is generally put in the form—

$$\beta = \frac{C_V}{Q_0 \left[1 - k \frac{E}{Q_0} \right]^2} \quad \text{..................(22)}$$

where Q_0 is a constant given by $V_0/\gamma K_0$ and k replaces $\frac{m+n+3}{6}$.

The Evaluation of γ

The frequency of the displaced atom can be put in the form

$$\nu = \frac{1}{2\pi} \sqrt{\frac{D}{\mu}} \quad \text{..................(23)}$$

where μ is the mass and D is the combined force constant due to the displacement of the atom relative to all its neighbours. D can be split up into two parts D_a and D_r arising out of attractive and repulsive forces respectively. γ, by definition, is given by

$$\gamma = -\frac{\partial \log \nu}{\partial \log V}$$

From equation (23)

$$\log \gamma = \text{cost.} + \tfrac{1}{2} \log D.$$

Hence
$$\frac{\partial \log \nu}{\partial \log V} = \frac{1}{2} \frac{\partial \log D}{\partial \log V}$$
$$= \frac{1}{2} \frac{\partial \log D}{\partial \log \bar{r}} \cdot \frac{\partial \log \bar{r}}{\partial \log V}$$
$$= \frac{1}{6} \cdot \frac{\partial \log D}{\partial \log \bar{r}} = \frac{1}{6} \quad \frac{\bar{r}}{D} \cdot \frac{\partial D}{\partial \bar{r}}.$$

where $\bar{r}$ is the mean distance between the two neighbouring atoms in the lattice.

Since the force constant between any two atoms is the second derivative of the potential energy, we have for the law of force (6).

$$\left. \begin{aligned} -\frac{\bar{r}}{D} \frac{\partial D_a}{\partial \bar{r}} &= \frac{(m+2) D_a}{D} \\ \text{and } -\frac{\bar{r}}{D} \frac{\partial D_r}{\partial \bar{r}} &= \frac{(n+2) D_r}{D} \end{aligned} \right\} \quad \text{..................(24)}$$

$$\text{so that } \gamma = \frac{1}{6} \left[\frac{(n+2) D_r + (m+2) D_a}{D} \right] \quad \text{..................(25)}$$

where the proper signs have to be put for D_r and D_a, and $D=D_a+D_r$. For ionic crystals and such others for which $n \geqslant m$ Gruneisen neglected D_a so that he obtained a constant value of γ equal to $(n+2)/6$.

Since the frequency corresponding to any mode of oscillation can always be expressed in the form (23), the above method of derivation of γ is quite general. If D_a is negligible compared to D_r for all the frequencies, there will be only one value of γ given by $\frac{n+2}{6}$ and the Gruneisen law will be valid. Generally, however, the term involving D_a is negligible in the numerator due to the factor $(n+2)$ in the term D_r, but this is not so in the denominator so that there is a different value of γ for each frequency.

DISCUSSION

From equation (21) it is obvious that Gruneisen, following Einstein, takes into account only one frequency of vibration of the crystal lattice and hence only one γ. Einstein himself recognised that the assumption of these "monochromatic vibrations" did not correspond to actual facts. The assumption that all the atoms can be regarded as oscillating about their positions of rest is far from truth in an actual body. The restoring forces tending to bring back a displaced atom in its position of rest are due to the neighbouring atoms, and for these to be directed towards the undisplaced position of a displaced atom and to be proportional to the displacement, it would be necessary for all the surrounding atoms to remain at rest in their undisturbed positions. Actually they are moving with the same type of motion as that of the atom which we are considering.

As is obvious, the motion of any particular particle will be very complicated indeed because it is under the field of force of numerous vibrating atoms. Nernst and Lindemann have found that the experimental result on specific heat can be satisfactorily explained if we assume that half of the number of vibrating atoms have frequency ν, and the other half have frequency $\nu/_2$. But there is no theoretical justification for this assumption.

The frequency distribution in the Debye theory of specific heats, on the other hand, is less successful in interpreting the thermal behaviour of many substances than was formerly supposed. For instance, the failure of the theory is very conspicuous in the case of even such cubic metals as gold, lithium and tungsten. But even for those substances where it had been previously thought to be adequate, systematic deviations from the Debye formula have been brought to light by new and more accurate measurements over a wide range of temperatures. These facts can scarcely be regarded as surprising when we consider the nature of the assumptions on which the theory is based and specially the fact that it does not take into account the details of the crystal structure of the solid, but regards it as a continuum.

Born and Karman, therefore, worked out the equations of motion for the atoms of the solid, assuming that the atoms interact only with their neigh and in accordance with Hooke's law. The nature of the frequency spectrum in the theory of Born is essentially determined by the "cyclic postulate". There are two sections to the theory namely, the acoustic and the optical branches. The frequencies in the acoustic branch increase continuously from zero to a limiting value in the short wave region. In the optical branch the frequency for great phase wave-lengths has a value approximately independent of such wave-length but generally falls off more and more rapidly with the diminishing wave-length, till it reaches minimum value at the short wave limit. The optical frequencies thus form a continuous spectrum extending between the limiting values of the frequencies corresponding respectively to the infinite and the smallest permissible wave-lengths. Blackman has extended Born's theory by assuming interaction not only with the immediate neighbours but also with the next immediate neighbours. His calculations are essentially qualitative but the importance of his theory lies in the fact that the specific heat of an actual crystal should not be expected to agree accurately with the Debye theory.

More recently Raman has reconsidered the problem of the lattice vibrations. His theory starts from the consideration of the theoretically possible normal modes of vibration of the atoms about their positions of equilibrium in the structure of the crystal. Raman has shown that there are (24p-3) modes of atomic vibration in a crystal where p is the number of non-equivalent atoms in the unit cell. The atomic vibration spectrum thus consists of (24p-3)[1] discrete or monochromatic frequencies, the number, however, being further diminished by degeneracy in the crystals possessing types of symmetry other than that of the translational kind.

Thus in all the later theories the vibration spectrum of a crystal consists of a large number of frequencies, each of which may have its own γ. These frequencies differ widely in their character and it is natural to suppose that their anharmonicities differ just as widely. This inference is amply justified by spectroscopic studies of light scattering in crystals at various temperatures. The results of such study in the case of two cubic crystals (sodium chlorate and ammonium chloride) whose thermal expansion has been studied by the present author are described and discussed below.

Further, according to Gruneisen theory, γ is a temperature independent quantity. It has also been shown thermodynamically that if we assume γ to be the same for all the frequencies, γ is independent of temperature even at low temperatures (Mott and Jones). From the results of experimental study by the author it is apparent that this assumption also is not borne out by experimental facts. γ, in the case of every crystal, exhibits marked variations with temperature throughout the whole temperature range.

Taken in conjunction with the Debye theory, the Gruneisen's formula, as embodied in equation (22), involves two arbitrary constants Θ and k, where Θ is the characteristic temperature giving specific heat and k is equal to

$\frac{m+n+3}{6}$. From a comprehensive review of the available data on thermal expansion by the author it has been revealed that the failures of the Gruneisen theory in the case of many crystals are intimately connected with the nature of their vibration spectra and we have no justification for assuming a single value of γ for all the vibration frequencies.

The incorrectness of this Gruneisen assumption can also be tested from a study of the vibration spectrum of a crystal as obtained from Raman effect studies. When the temperature of a crystal is raised the atoms get less tightly packed, resulting in an increase in the interatomic distances and corresponding diminution of the forces acting on them. The frequencies of atomic vibrations which are determined by the interatomic forces will therefore be diminished. It is obvious that these frequency changes would in turn be related to the thermal expansion of the crystal. Thus, according to definition

$$\gamma_j = -\frac{\partial \log \nu_j}{\partial \log V} = \frac{1}{\nu_j} \cdot \frac{\Delta \nu_j}{\Delta T} \cdot \frac{1}{3\bar{\alpha}} = \frac{\xi_j}{3\bar{\alpha}}.$$

where $\Delta\nu_j$ is the diminition in frequency ν_j in the temperature range ΔT and $\bar{\alpha}$ is the mean coefficient of linear expansion in the same range. ξ_j is substituted for the expression $\frac{1}{\nu_j} \cdot \frac{\Delta \nu_j}{\Delta T}$. Thus, the above equation affords a means of calculating the Gruneisen constants of different frequencies of the vibration spectrum. Below are given such calculations for two crystals – $NaClO_3$ and NH_4Cl – whose thermal expansion has been studied by the present author and for which data on temperature variations of Raman frequencies are also available from the spectroscopic studies by Shanta Kumari and Krishnan respectively.

TABLE I. Sodium chlorate. Frequency dependence of Gruneisen's constant

Raman frequency (ν_j)	Shift for (300—513)° K ($\Delta\nu_j$)	$\xi_j \times 10^6$	$\bar{\alpha} \times 10^6$	γ_j
76.5	6.3	392.7	52.37	2.5
127	9.1	336.3	,,	2.1
179	7.0	183.5	,,	1.2
625	5.3	39.66	,,	0.25
966	3.8	18.48	,,	0.12
984	5.3	25.28	,	0.16
1028	6.2	28.32	,,	0.18

TABLE II. Temperature dependence of the Gruneisen's constant for the different Raman frequencies

Raman frequency (ν_j)	Temperature range (°K)	Frequency Shift $(\Delta\nu_j)$	$\xi_j \times 10^6$	$\bar{\alpha} \times 10^6$	γ_j
76.5	300/373	2.1	385	46.98	2.7
	373/453	2.4	892	52.68	2.5
	453/513	1.8	403	53.57	2.3
127	,,	3.3	323.6	,,	2.3
		3.5	344.5		2.2
		2.3	341.0		1.9
984	,,	1.8	25.1	,,	0.18
		2.0	25.3		0.16
		1.5	24.6		0.14
1028	,,	2.1	28.4	,,	0.20
		2.4	28.5		0.18
		1.7	28.3		0.07

The average Gruneisen's constant γ as obtained from thermal expansion measurements varies from 1.55 to 1.68 in the temperature range (303-513)°K.

Ammonium Chloride

In the case of this crystal the measurements on frequency shift are not so accurate as in the case of sodium chlorate due to extreme broadening of the lines at elevated temperatures. Hence no calculations on the temperature dependence of the Gruneisen's constant are attempted; only the separate γ's are evaluated for different frequencies over an extended range of temperature from 268°K to 395°K.

TABLE III Frequency dependence of Gruneisen's constant

Raman frequency (ν_j)	Frequency shift $(\Delta\nu_j)$	$\xi_j \times 10^6$	$\bar{\alpha} \times 10^6$	γ_j
92	5	428.0	71.24	2.00
141	7	390.9	,,	1.83
170	12	555.9	,,	2.60
195	15	605.7	,,	2.83

From the thermal expansion measurements the mean value of γ comes out to be 1.48. A comparison of this value with the values of γ_j entered in the last column of the above table indicates that it does not fall in line with any of them. The discrepancy can partly be accounted for by the error involved in the measurements of $\Delta\nu$ at higher temperatures. But the main cause appears to be the approximations employed in the evaluation of γ. For instance, the values of compressibility and molecular volume should be those at 0°K and under zero external pressure. The value of the former may vary considerably from the room temperature value. As for example, Slater's values for the compressibilities of various alkali halides indicate that the difference in the values of χ_{30} and χ_0 ranges from 15-25% In the case of NH_4Cl Bridgman's value for χ_{30} is $6{\cdot}02 \times 10^{-12}$ cm^2/dyne; while that given by Bleick at 0°C is 5.76×10^{-12} cm^2/dyne, so that if the value of compressibility be extrapolated to absolute zero, it may differ by more than 25% from the room temperature value. This assumption yields a value of γ equal to 1.85 which falls in between the values for γ_j in the above table.

Thus it is obvious that the systematic deviations from the Gruneisen's relation are due to the assumptions on which the theory is based.

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SYNTHESIS OF SOME PHENOXAZINES

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Phenoxazine was first prepared by condensing o-amino-phenol with catechol (1,3). Nitro phenoxazines were obtained by warming poly nitro anisole and o-amino-phenol with alcoholic caustic potash (6, 7). Some substituted nitro phenoxazines were obtained by condensing o-amino-phenol with a number of aromatic compounds containing a reactive halogen (4,5).

In the present investigation a number of phenoxazines have been prepared by condensing 6-amino-o-cresol, (3-amino-2-hydroxy I-methyl-benzene) 2-amino-p-cresol (3-amino-4-hydroxy-I-methyl benzene) and 2-amino-4 6 dibromo-phenol with 1-chloro-2:4 dinitro-benzene, 4-chloro-3:5 dinito-benzoic acid and 1-bromo-2:4 dichloro-3:5 dinitro benzene.

EXPERIMENTAL

Preparation of Phenoxazines :—

Equimolecular quantities of appropriate amino phenolic compound (A) and active hlogen componnd (B) were taken with a sufficient quantity of sodium acetate and alcohol. They were refluxed on a water bath for several hours. The liquid soon darkened and dark coloured solid product separated out. It was crystallised from different solvents.

The system of numbering as given in Beilstein's Hand buchder organischm chemie has been followed.

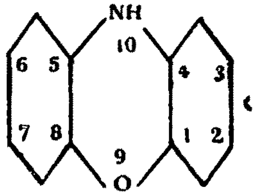


Table I

Phenoxazines formed by the condensation of o-amino-phenolic compound with active halogen aromatic compounds.

Expt. No.	Amino-phenolic compound (A)	Active halogen compound (B)	Phenoxazines formed	M. P.	Analysis
1.	2	3	4	5	6
1.	2-amino-4:6 di-bromo phenol.	1-Bromo-2:4 di-chloro-3:5-dinitro benzene.	1 (or 3) chloro-4-nitro-2:6:8 tri-bromo-phenoxazine. ($C_{12}H_4O_3N_2Br_3Cl$)	240°C.	Found Cl+Br 55'5% Cal 55'1%

1.	2	3	4	5	6
2.	6-amino-o-cresol (3-amino-2 hydroxy-1-methyl benzene)	-do-	1 (or3) chloro-2-Bromo-4-nitro 8-methyl-phenoxazine ($C_{13}H_8O_3N_2Cl\ Br$)	220°C.	Found Cl+Br 33'12% Cal 32'5%
3.	2-amino-p-cresol (3-amino-4 hydroxy-1-methyl benzene)	-do-	1 (or 3) chloro-2-bromo-4-nitro 6-methyl-phenoxazine. ($C_{13}H_8O_3N_2ClBr$)	212°C.	Found Cl+Br 32'08% Cal 32' 5%
4.	2-amino-4:6-dibromo-phenol	1-chloro-2:4-dinitro-benzene	2-nitro-6:8-dibromo-phenoxazine ($C_{12}H_6O_3N_2Br_2$)	262°(d)	Found Br 41'0% Cal 41'4%
5.	2-amino-4:6-dibromo-phenol	4-chloro-3:5-dinitro-benzoic acid.	2-carboxy-4-nitro-6:8 dibromo-phenoxazine ($C_{13}H_6O_5N_2Br_2$)	280°(d)	Found Br36'4% Cal 37'2%
6.	2-amino-p-cresol	-do-	2-carboxy-4-nitro-6-methyl phenoxazine. ($C_{14}H_{10}O_5N_2$)	Above 300°(d)	Found Eq. Wt 285'5 Cal. 286.

The phenoxazines give different colours with boiling caustic soda and sulphuric acid.

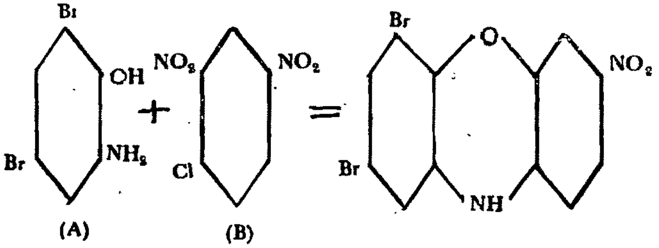
Table II

Colour given by different phenoxazines with caustic soda and sulphuric acid.

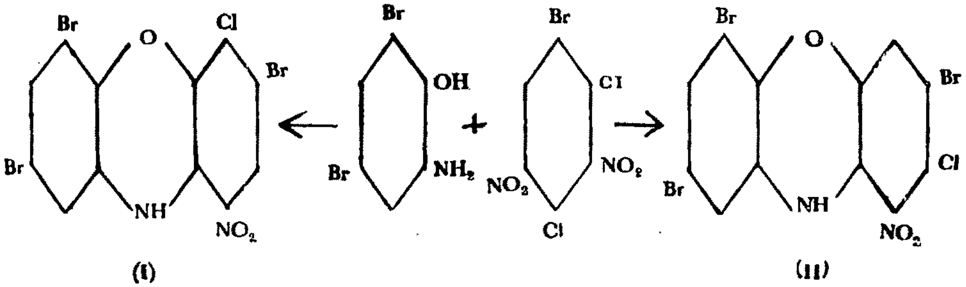
Expt. No.	Name of the compound.	Colour of the compound	Colour with caustic soda boiling.	Colour with sulphuric acid	
1	2	3	4	5	
				Conc.	on dilution
1.	1 (or 3) chloro-4-nitro-2:6:8-tribromo-phenoxazine.	Dark Violet	...	Pink	No change.
2.	1 (or 3) chloro-2-bromo-4-nitro 8-methyl phenoxazine.	Purple	Light pink	Purple	Red.
3.	1 (or 3) chloro-2-bromo-4-nitro-6-methyl-phenoxazine.	Dark violet	...	Violet	Red. (dirty)
4.	2-Nitro-6:8 dibromo-phenoxazine.	Red.	...	Navy blue	Light orange
5.	2-carboxy-4-nitro-6:8-dibromo-phenoxazine.	Blue violet.	Dirty brown	Light Yellow	Light orange.
6.	2-carboxy-4-nitro-6-methyl-phenoxazine.	Black.	Dark Red.	Dirty orange.	Yellow.

DISCUSSION

The amino group of amino-phenol reacts with one of the active halogen atoms and subsequently, the (OH) group phenolic removes the adjacent nitro group, yielding a phenoxazine derivative. Phenoxazines obtained from 1-chloro-2:4 dinitro-benzene and 4-chloro-3:5-dinitro-benzoic acid have definite structures.



In case of 1-bromo-2:4 dichloro-3:5-dinitro-benzene, the chlorine atom in position 4 reacts with the amino group of o-amino-phenol because usually a halogen atom, which has two nitro groups in both of its o-positions, is more reactive than the one which has the nitro groups in its o-p-positions (2). The phenoxazines that is finally formed may have either structure (I) or (II) according as the nitro group of position 3 or 5 is removed.



SUMMARY

Preparation of six different phenoxazines obtained by the condensation of 6-amino-o-cresol (3-amino-2-hydroxy-1-methyl benzene), 2-amino-p-cresol (3-amino-4 hydroxy-I-methyl benzene) and 2-amino-4:6 dibromo-phenol with 1-chloro-2:4 dinitro-benzene, 4-chloro-3:5 dinitro benzoic acid and 1-bromo-2:4 dichloro-3:5 dinitro-benzene has been described.

The author is grateful to Dr. S. S. Joshi, D. Sc., Vice.Principal and Head of the Chemistry Department, Meerut College, and to Dr. O. N. Perti, M. Sc., D. Phil., Head of the Chemistry Department, D. S. B. Government College, Nani Tal, for taking keen interest throughout the work.

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CHANGES IN TOTAL CATION EXCHANGE CAPACITY IN 'DUMAT' SOIL OF AGRA DISTRICT BY HUMIFYING THE LEGUMES, (1) ZOONZHRU (MELILOTUS INDICA) (2) KANJI (PONGAMIA GLABRA) AND NON-LEGUME,—AROUSA (JUSTICIA ADHOTODA)

By B. R. Nagar and Abani K. Bhattacharya, *Professor of Chemistry, Agra College, Agra.*

Parker and Pate (1926) observed that the exchangeable base in soil appears to remain in the colloidal material, because a good correlation between SiO_2/R_2O_3 ratios of soil colloids and their contents of exchangeable bases was obtained. Williams (1932) studied the contribution of clay and organic matter to the base-exchange capacity and showed that the base-exchange capacity was the most complicated function of clay content than is merely given by the ratio SiO_2/R_2O_3 and further suggested that the chemical characteristics of structural influence was probably involved in the base-exchange phenomenon. The relation between the organic matter in the soil and base-exchange capacity has been studied by many workers. McGeorge (1934) studied the base-exchange in presence of plant residues and green manures and came to the definite conclusion that base exchange capacity increases in presence of these substances. Smolik (1933) observed that the Ligno-humus constituents of different soils do not show the same exchange capacity and it quickly rises with the progressive humification. Miller and Co-workers (1936) observed that the decomposition of leguminous materials increased the exchange capcity of the Dickenson fine sandy loam more than the non-leguminous bodies. Baver (1930) studied the effect of organic matter on several physical properties of soils and observed that exchange capacity of humus varies between wide limits but usually is in the range of 100 to 300 M.E. per 100 grams.

In view of the foregoing references it is obvious that opinion regarding the relation of base-exchange property, organic matter and SiO_2/R_2O_3 ratio should be further elaborated by more extensive data. With this end in view we have carried out some experiment on the humification of two legumes:— Zoonzhru and (2) Kanji and non-legume:—Arousa, in the 'Dumat' soil of Agra district to determine the nature of correlation observed between variations in SiO_2/R_2O_3 ratio, the residual organic matter against the changes in cation exchange capacity brought about by the humification of these plants for the period of 16 weeks.

Experimental

The dirt was removed from the plants and they were crushed, pulverised and sieved through 100 mesh sieve. The raw organic matter in this form was mixed with the soil and the whole quantity was macerated with distilled water and left under the shade to humify The moisture content of the soil was maintained at 15% by weighing in a Beringer's balance on alternate days and adding required amount of distilled water. At the end of 16 weeks soil samples were taken out and air dried. The soil samples thus obtained were properly sieved (100 mesh). The average of the four replicas is given in the table. Inorganic constituents of the plants were estimated by the methods suggested by A.O.A.C. (1945). Total cation exchange capacity was determined by the method suggested by Piper (1947). Organic carbon was determined by Walkley's (1935) rapid titration method.

TABLE No. 1

Analysis of soil and organics added for humification

	Soil sample	*Zoonzhru*	*Kanji*	*Arousa*
Loss on Ignition.	3.149%	85.412%	85.64%	88.86%
Sand	82.726%	4.246%	2.9304%	1.2452%
Alkali Soluble silica.	—	1.5960%	2.1912%	1.0364%
Fe_2O_3	4.2795%	0.511%	0.0405%	0.1570%
CaO	3.238%	3.537%	2.073%	2.615%
MgO	1.8375%	0.7754%	1.108%	0.7082%
Al_2O_3	3.5604%	1.5935%	2.067%	1.3851%
K_2O	1.483%	1.8170%	2.846%	2.492%
P_2O_5	0.1201%	0.3495%	0.5758%	0.4916%
SiO_2/R_2O_3 ratio	—	5.173	4.173	2.615

TABLE No. 2

Changes in total cation exchange capacity in the 'Dumat' soil of Agra district by humifying the legumes, Zoonzhru and Kanji and non-legume, Arousa.

(For 16 Weeks)

Soil sample	% organic matter added	Total cation exchange capacity.	Organic carbon.	SiO_2/R_2O_3 ratio of the plant taken for humification.
Untreated soil	—	5.5 m.e.	0.2923%	—
Humified with Zoonzhru.	20%	14.5 m.e.	3.833%	5.173
Humified with Kanji (Legume)	5%	6.75 m.e.	1.245%	4.173
Humified with Arousa (Non-legume)	5%	7.5 m.e.	1.189%	2.615

Discussion

From the data given in the table No. 2 the following important observations can be made regarding the variations in total cation exchange capacity, SiO_2/R_2O_3 ratio of the plant and also the residual percentage of organic carbon left in the soil after 16 weeks of humification.

The total cation-exchange capacity of the soil after humification does not depend upon the leguminous or non-leguminous nature of plants as observed by Miller and Co-workers (1936). This observation is borne out by the fact that Arousa non-leguminous has greater total cation exchange capacity (7.5 m.e.) than leguminous Kanji (6.75).

Total cation exchange capacity neither seems to depend exclusively upon the SiO_2/R_2O_3 ratio of the plant nor on the residual organic matter taken as single factors e.g. in the case of Kanji the total cation exchange capacity is the lowest where SiO_2/R_2O_3 ratio of the plant was slightly less than the Zoonzhru and where the added organic matter was also considerably reduced. The fall in total cation exchange capacity can be possibly due to both of these factors. In the case of Arousa where SiO_2/R_2O_3 of the weed and also of the residual carbon were considerably less, the total cation exchange capacity was, however, found to be a little greater than Kanji. Such an observation reveals that the cation-exchange capacity of the humified soil is a more complicated function of the colloidal clay humus complex and the physico-chemical characteristics arising out of its structure. Since the physico-chemical characteristics depend upon the structure of the clay mineral and the character of the humus formed, it appears that the cation exchange capacity may ultimately depend on the relative predominance of the characteristics of the clay mineral over those of the humus content, and vice-versa. $\frac{SiO_2}{R_2O_3}$ ratio is only one of so many factors which may control the base exchange phenomenon.

Summary

Two legumes, Kanji and Zoonzhru and one non-legume, Arousa were humified (for 16 weeks) in the 'Dumat' soil of Agra district and the changes in total cation exchange capacity, residual organic carbon and SiO_2/R_2O_3 ratio of the plants were studied.

It has been suggested that total cation exchange capacity depends on the factors, (1) clay-humus complex and physico-chemical characteristics arising out of its structure (2) Structure of the clay mineral and (3) SiO_2/R_2O_3 ratio of the plant. The predominance of SiO_2/R_2O_3 over the other factors, or vice versa finally controls the total cation exchange capacity of humified samples. It is further suggested that the changes in total cation exchange capacity in 'Dumat' soil by humifying the plants is independent of their leguminous or non-leguminous nature.

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REACTIONS OF HALOGEN SUBSTITUTED—BROMO ACETOPHENONES

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In order to explain the anomalous behaviour of some bromo oxymethylene ketones the present investigation of the reactions of halogen substituted-halogenated acetopenones was undertaken. A variety of products have been reported by the action of alkali on phenacyl bromide. Thus Fritz (5) obtained α & β-diphenacyls by the action of alkali on α-Bromo-acetophenone. Tommass Ajello (15) obtained γ-bromo-diphenacyl i.e. 1-bromo-1:2 dibenzoyl ethylene by the action of caustic soda on α-bromo acetophenone. B.M. Bogoslovkii (3) prepared 1:2 dibenzoyl ethylene by the action of warm aquous caustic potash on α-bromo acetophenone in alcohol. Fuson and Johnson (6) were unable to prepare 1:2 di (2:4:5 trimethyl) benzoyl ethylene by this reaction. Neil Campbell and Nando Mal Khanna (14) successfully applied Bogoslovkiis method to the preparation of 1:2 dibenzoyl ethylenes. But they failed to prepare 1:2 di (p-nitro benzoyl) ethylene. The diversity of the results led us to a thouorgh investigation of the action of alkali under varied conditions (details in experimental part). We studied the action of alkali on α-halogenated acetophenones under three different conditions. The results obtained are recorded in table I, II & III of the experimental part. With alcoholic caustic potash p-bromo-phenacyl bromide undergoes inverse substitution giving p-bromo-acetophenone (Cf. action of alkali on dibromo (18,19) and bromo camphor (20, 21). In the cases studied with aquoeus alkali dibenzoyl ethylenes were the sole products. Boiling alkali brings about cleavage of the ketone forming carboxylic acid (4, 7, 8). In case of Bromo-oxymethylene acetophenone boiling alkali gave benzoyl formic acid.

α-Halogenated ketones when treated with acidified potassium iodide solution liberated iodine (10, 11, 17). The quantitative nature of the reaction forms the basis of enol estimation by K. H. Meyer s method (12, 13) and it has been independently verified by Bokadia and Deshapande (2) and Bokadia (1). In the present study we took nuclear substituted α-halogenated ketones. The results are recorded in table IV experimental part. From the results it is evident that the nuclear halogen remains intact during inverse substitution. After inverse substitution ketones free from α-halogen atom are regenerated.

From the results recorded in table No. III and IV it is evident that in reactions with boiling alkali and in inverse substitution α-Bromo Ketones and Bromo Oxymethylene Ketones behave alike. But they differ in their reaction towards alcoholic and aqueous alkali in cold as shown by the results in table

I and II. This difference may be attributed to the oxymethylene structure in the case of Bromo oxymethylene acetophenone. But in the case of ordinary α-Bromo Ketones the oxymethylene form is practically absent.

EXPERIMENTAL

Reaction with cold alcoholic caustic potash.

Bromo acetophenone (nearly 2 g.) was dissolved in alcohol (10 c.c.) and to this alcoholic caustic potash (caustic potash .5 g., water .4 c.c. and ethyl alcohol 25 c.c.) was added gradually with vigorous shaking. After five minutes the mixture was poured in 40 c.c. of water. The product formed was extracted with ether. The ethereal extract was washed with water dried over fused calcium chloride and ether recovered. The product was crystallised with proper solvent and analysed. The results obtained are recorded in table I.

Table I

No.	Compound	Product	M. P. with different solvents	Analysis
1	2	3	4	5
1.	Phenacyl bromide	1:2 dibenzoyl ethylene	(a) Alchol, yellowish, M.P. 134°C (cis) (b) Benzene, yellow, M.P. 111°C (trans).	(cf. 14)
2.	p-bromo phenacyl bromide	p-bromo acetophenone	White, M.P. 50°C.	2:4 dinitro phenyl hydrazone M. P. 233°O mixed M.P. 233°C
3.	p-chloro-phenacyl bromide	1:2 di (p-chloro benzoyl) ethylene.	(a) Benzene, yellowish, M.P. 172°C. (trans). (b) Chloroform, yellowish M.P. 102°C(cis)	(Cf. 10, 11)
4.	α-Formyl- α-bromo acetophenone.	No Change		

Reaction with cold aqueous caustic potash:

Bromo acetophenone (3 g.) was dissolved in ethyl alcohol (95%, 10 c.c.) and to this added aqueous caustic potash (·65 g. in 1.5 c.c. of water) very slowly with constant shaking. After two hours it was diluted with 2.5 c.c. of water and left over night. On the next day it was further diluted with 1 c.c. of water. The product after filtration was washed with cold alcohol, cold water and then with hot water and crystallised. The results are shown in table II.

Table II

No.	Compund	Product	M. P. with different solvents	Analysis
1	2	3	4	5
1.	Phenacyl Bromide	1:2 dibenzoyl ethylene.	(a) Alcohol, yellowish, M. P- 134°C. (cis) (b) Benzene, yellow, M. P. 111° (trans)	(cf. 14)
3.	p-bromo phenacyl bromide	1:2 di (p-bromo-benzoyl) ethylene	(a) Absolute alcohol, yellow M.P. 92°C. (b) Benzene, yellow, M.P. 162°C	Found Br 40·5% Cal 40·6%.
3.	p-chloro phenacyl bromide.	1:2 di (p-chloro benzoyl) ethylene	(a) Benzene, yellowish, M.P. 172°C (trans) (b) Chloroform, yellowish M.P: 102°C (cis)	(cf. 10, 11)
4.	α-formyl- α bromo	No change.		

Reaction with boiling alkali:—

To bromo acetophenone (4 g.) dissolved in alcohol (10 c.c.) was added aqueous caustic soda (4 g. in 15 c.c. of water) and the mixture was refluxed for an hour on sand bath under an air condenser. After the reaction it was extracted with ether. The ethereal mixture was washed with water, dried over fused calcium chloride and ether recovered. The product was crystallised.

The aqueous alkaline solution left after ether extraction was acidified with dilute hydrochloric acid. The precipitate obtained was crystallised and the product was identified by its M.P., mixed M.P. (where ever possible) with an authentic sample and determination of eq. wt. The results are given in table III.

Table III

No.	Compound	Product obtainedfrom ethereal extract.	Acid obtained	Neutralisation, equivalent
1.	2	3	4	5
1.	Phenacyl bromide	1:2 dibenzoyl ethylene	Benzoic acid M.P. 121°C Mixed M.P. 121°C.	Found 121.8 Cal. 122.0.
2.	p-bromo phenacyl bromide	1:2 di (p-bromo benzoyl) ethylene.	p-bromo benzoie acid M.P. 251°C.	Found 199'9. Cal. 201.0.
3.	p-chloro phenacyl bromide	1:2 di (p-chloro benzoyl) ethylene.	p-chloro benzoie acid M.P. 234°C Mixed M.P.234°C.	Found 155.1 cal. 156.5.
4.	α-formyl- α-Bromo acetophenone	Gummy product	Benzoyl formic acid M.P. 66°C	Found 149.5 cal. 150.

Weighed (·5 g.) amount of bromo acetophenone was dissolved in alcohol (20 c.c.) and to this aqueous potassium iodide solution (2 g. in 5 c.c.) and dilute sulphuric acid (5 c.c.) were added. The mixture was warmed. The liberated iodine was titrated against standard hypo-solution. After titration the product was extracted with ether. The ethereal extract on recovery of ether gave a product which was identified by the melting point of its semicarbazone or 2:4 dinitro-phenyl hydrazone and mixed M.P. of these derivatives. The results are recorded in table IV.

Table IV

No.	Compound	Weight of substance.	Strength of Hypo solution.	Titre value	Iodine liberated by I mol.	Product recovered after inverse substitution.
1	2	3	4	5	6	7
1.	Phenacyl bromide	·3490 g.	N/9.2	32.85c.c.	·99 Mol.	Acetophenone.
2.	p-chloro-phenacyl bromide	·2328 g,	-do-	15.3 c. c.	·99 Mol.	p-bromo acetophenone.
3.	p-chloro-phenacyl bromide	·1500 g,	-do-	11.6 c. c.	·98 Mol.	p-chloro acetophenone.
4.	α-formyl- α-bromo actophenone.	·184 g.	-do-	16.3 c. c.	·99 Mol.	Sym.tri benzoyl benzene.
5.	Bromo camphor	Does not liberate iodine.				

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USE OF GRIGNARD REAGENT FOR THE DETERMINATION OF ENOL IN HYDROXYMETHYLENE KETONES

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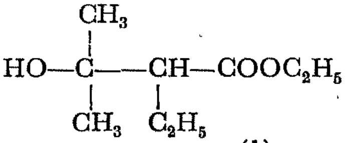
Grignard's reagent reacts with an active hydrogen compound producing a hydrocarbon and an organo-metallic complex. The latter on decomposition with water will generate the original compound. Tschugaeff and Zerevitinoff (10) developed an experimental technique for the estimation of active hydrogen in organic compounds by measuring the volume of the evolved hydrocarbon from a known weight of the compound. Grignard (6) has shown that magnesium methyl iodide reacts with ethyl aceto acetate evolving methane. On the other hand monoethyl derivative of the ester gave β—hydroxy α ethyl isovalerate (I) showing that the ethyl derivative is purely ketonic, while there is no action of the reagent whatsoever on the diethyl derivative of the ester. In contrast to the mono ethyl derivative which



$$HO-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{C_2H_5}{\underset{|}{CH}}-COOC_2H_5$$

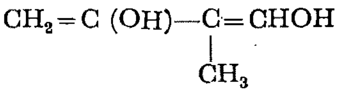
(1)

behaves as purely ketonic it has been found by Mc Kenzie (9) that the methyl derivative of the ester behaves towards Grignard reagent as if it is entirely enolic. Hepworth (7) treated diesters of dicarboxylic acids with Grignard's reagent to find out their enolic character.

All these observations are qualitative in nature, the aim being to diagonise whether the group $O=\overset{|}{C}-\underset{|}{CH}-$ in the molecule behaves as $-\overset{|}{C}(OH)=\overset{|}{C}-$. Hiebert and Sudborough (8) made quantitative observation of the volume of methane evolved when excess of magnesium methyl iodide is allowed to remain in contact for prolonged period, with a weighed amount of the carbonyl compound. In the case of ethyl aceto acetate the volume of methane evolved was found to be almost equal to the culculated volume for 100% enolic structure. In the case of desoxy benzoin even after prolonged contact with the reagent the volume of methane evolved was only 1/10th of the volume corresponding to completely enolic structure. Bhagvat and Sudborough (I) also observed that the reagent favours enolization

If the period of contact between the reagent and the keto-enol equilibrium mixture is shortened, the volume of methane evolved can be approximately a measure of the enol content of the mixture. This measure can be only approximate because it is not easy to say how much should be the required period of contact. Different enols will require different periods. If the period is shorter than the required period, the reaction will be incomplete, and the values obtained will be low. If it is longer, the reagent will induce further enolization and values of enols will be too high.

If one plots a graph of the volume of methane evolved against time of contact between the mixture and the reagent one is expected to observe a steep rise in the curve during the initial few seconds followed by further slow rise. The maximum of the steep rise corresponds to the enol initially present in the equilibrium mixture and the rate of further rise corresponds to the rate of enolization induced by the reagent. Following this procedure the enol content of some oxymethylene ketones have been determined and the values so obtained agree well with the results obtained by other methods (2, 3, 4, 5.) It also provides an evidence for the existence of dienolic form (II) of oxymethylene methyelthyl ketone.



$$CH_2=C\,(OH)-\underset{\substack{|\\ CH_3}}{C}=CHOH$$

(II)

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STUDIES ON THE COMPOSITION AND COLLOIDAL BEHAVIOUR OF THE FERROCYANIDE OF SOME METALS

PART II—THE HYDROLYTIC AND ADSORPTIVE PROPERTIES OF COBALT FERROCYANIDE SOL IN THE LIGHT OF ITS COMPOSITION BY PHYSICOCHEMICAL METHODS.

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AND

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The hydrolysable and adsorptive character of cobalt ferrocyanide has been investigated by precipitating cobalt ferrocyanide sol. Estimations of free ferrocyanide in the undialysed and dialysed samples of the sol at various dilutions and at different temperatures give evidence of hydrolysis in the freshly precipitated complex. Experiments on adsorption show that both $FeCy_6^{----}$. and Co^{++} are adsorbed by freshly precipitated cobalt ferrocyanide.. The results on hydrolysis and adsorption lend support to the views put forward on the composition of the complex in Part I of this paper.

In our previous communication on the composition of cobalt ferrocyanide by conductometric, potentiometric and thermometric methods, the discrepancy between the theoretical and observed titre values both for direct (when $CoCl_2$ was added to K_4FeCy_6) and reverse (when K_4FeCy_6 was added to $CoCl_2$) titrations was explained on the basis of adsorption effects and the hydrolysable character of the freshly precipitated complex. In the light of the above observation, it was deemed necessary to investigate the hydrolytic character and adsorptive properties of the compound.

The present communication describes the experiments on the effect of dilution on cobalt ferrocyanide and those on the adsorption of K_4FeCy_6 and cobalt chloride by the freshly precipitated complex.

EXPERIMENTAL

Preparation of cobalt ferrocyanide sol. In order to prepare the sol, the following solutions were prepared in doubly distilled water and their strengths determined.

1. $K_4Fe(CN)_6$ solution—111.2gms. per litre (estimated volumetrically against $KMNO_4$ solution of known strength).

2. $CoCl_2$ solution—64.945 gms. per litre (estimated gravimetrically as $CoNH_4PO_4$).

The strengths of the solutions being known, the amounts of cobalt chloride and potassium ferrocyanide required to precipitate 2.5 gms. of cobalt ferrocyanide were calculated from the following equation.

$$CoCl_2+K_4Fe(CN)_6=K_2CoFe(CN)_6+2KCl$$

500 c.c. of cobalt ferrocyanide sol of strength 2.5 gms. per litre was then prepared by mixing 14.8 c.c. of potassium ferrocyanide solution (111.2 gms/litre) to 7.15 c.c. of cobalt chloride (64.945 gms/litre) in the proportion of 1 : 5/4 equivalents. The ferrocyanide solution was mixed gradually followed by stirring. A sol was formed which was dialysed in for several days.

In order to carry out hydrolysis experiments, the following procedure was adopted.

The undialysed and dialysed sols were taken and diluted with distilled water. Sols of four concentrations A; A/2; A/4; and A/8 were prepared by dilution, A being the initial concentration of the sol. The sols were precipitated by amonium sulphate, and the clear supernatant liquid was titrated against dilute standard solutions of potassium permanganate. The experiments on the undialysed were carried out at 15°C and 35°C. The results are summarised in the following table.

Table I

Cencentration of the sol. in gms./litre	Amount of K_4FeCy_6 in gms. in 25 c.c. of the sol.	Amount of K_4FeCy_6 in gms. released per gms. of the sol.	Amount of K_4FeCy_6 in gms. per 100 gms. of the sol.	Increase of K_4FeCy_6 in gms. on dilution
Undialysed sol.				Temp. 15°±0.1°C
2.50	0.01146	0.1833	18.33	...
1.25	0.00623	0.1993	19.93	1.60
0.625	0.00346	0.2214	22.14	2.21
0.3125	0.00184	0.2362	23.62	1.48
				Temp. 35°±0.1°C
2.50	0.01292	0.2067	20.67	...
1.25	0.00692	0.2214	22.14	1.47
0.625	0.00392	0.2488	24.88	2.74
0.3125	0.00208	0.2658	26.58	1.70
Sol Dialysed for. one day				Temp. 35°±0.1°C
2.5	0.00828	0.1324	13.24	...
1.25	0.00460	0.1466	14.66	1.42
0.625	0.00276	0.1764	17.64	2.98
0.3125	0.00138	0.1764	17.6	...
Sol. dialysed for three days				Temp. 35°±0.1°C
2.50	0.007615	0.1218	12.18	...
1.25	0.003920	0.1254	12.54	0.36
0.625	0.002077	0.1329	13.29	0.75
0.3125	0.001153	0.1475	14.75	1.46
Sol. dialysed for four and five days				Temp. 35°±0.1°C
2.50	0.006920	0.1107	11.07	...
1.25	0.003692	0.1181	11.81	0.74
0.625	0.001846	0.1181	11.81	...
0.3125	0.000923	0.1181	11.81	...

For adsorption experiments dialysed sols were taken and five cylinders were arranged in series containing the following mixtures of CoCl2 and cobalt ferrocyanide sol.

(1) 25 c.c. of the sol.+25 c.c. water.
(2) 25 c.c. of the sol.+25 c.c. M/12.25 $CoCl_2$ solution.
(3) 25.0 c.c. of the sol.+25.0 c.c. M/8.96 $CoCl_2$
(4) 25.5 c.c. of the sol.+25 c.c. M/6.12 $CoCl_2$
(5) 25.0 c.c. „ „ +25.0 c.c. M/4.9 $CoCl_2$

Before estimating the adsorption of cobalt chloride by the sol, it was found necessary to estimate whether any free $K_4Fe(CN)_6$ was present in the dialysed sol. In order to ascertain this, ammonium sulphate was added to the sol in the first cylinder and left for twenty four hours. The supernatant liquid obtained after the coagulation of the sol was then titrated against N/324.8 $KMn0_4$ solution. It was found that only a drop of $KMn0_4$ when added to 10. c.c. of the supernantant liquid was sufficient to give a pink colour. Hence the quantity of free ferrocyanide was taken to be negligible in the dialysed sol. The amounts of $CoCl_2$ adsorbed were determined in each cylinder by estimating the concentrations of $CoCl_2$ before and after adsorption under the same conditions of dilution. The amounts adsorbed were obtained difference.

The results on the adsorption of $CoCl_2$ by cobalt ferrocyanide have been summarised in Table No. II and have been represented graphically in Fig. 2.

Table II

Vol. of the sol. and electrolyte	Wt. of the adsorbent in gms.	Wt. of $CoCl_2$ be- before adsorption in gms.	Wt. of $CoCl_2$ be- after adsorption in gms.	Amount adsorbed in millimoles per litre	Equlibrium Conc.
50 c.c.	0.0625	0.4848	0.4692	1.012	9.395
„	„	0.7270	0.6610	4.437	13.22
„	„	0.9695	0.8530	7.654	17.06
„	„	1.2150	1.0700	9.747	21.40

The adsorption of potassium ferrocyanide by cobalt ferrocyanide was determined in the same manner as that used for $CoCl_2$. Five cylinders were arranged containing the following mixtures.

(1) 25.0 c.c. of the sol.+25.0 c.c. of M/60 $K_4Fe(CN)_6$
(2) 25.0 c.c. of the sol.+25.0 c.c. of M/40 ”
(3) 25.0 c.c. of the sol.+25.0 c.c. of M/30 ”
(4) 25.0 c.c. of the sol.+25.0 c.c. of M/20 ”
(5) 25.0 c.c. of the sol.+25.0 c.c. of M/10 ”

The sols in the cylinders were then coagulated by adding ammonium sulphate. The supernatant liquid was then titrated against standard potassium permanganate solution. The amounts of K_4FeCy_6 adsorbed were then obtained by the difference of the concentrations of K_4FeCy_6 before and after adsorption.

The results on the adsorption of $K_4Fe(CN)_6$ by cobalt ferrocyanide have been summarised in Table III. These have also been graphically represented in Fig. 3.

Table III

Vol. of the sol and electrolyte	Wt. of the adsorbent in gms.	Wt. of K_4FeCy_6 before adsorption in gms.	Wt. of K_4FeCy_6 after adsorption in gms.	Amount adsorbed in millimoles per litre	Equlibrium conc.
50.0 c.c.	0.0625	0.1530	0.1473	0.2447	2.2946
,,	,,	0.2314	0.2229	0.3671	4.458
,,	,,	0.3069	0.2974	0.4127	5.918
,,	,,	0.4605	0.4486	0.5172	8.971
,,	,,	0.9205	0.9055	0.6082	13.13

DISCUSSION

The following interesting points arise out of our observations on hydrolysis studied by estimating the free ferrocyanide in the dialysed and undialysed samples of cobalt ferrocyanide sols at different dilutions and at different temperatures.

1. Temperature effect is more pronounced in the case of undialysed sol than in the dialysed one, in as much as it shows no temperature effect after the first day of dialysis within the range of 20° C (Vide Table No. I and Fig. No. I).

2. Another striking point is the linearity or non-linearity of the curves. It will be observed that the dilution effect on the undialysed sol. is linear, showing that the amounts of free ferrocyanide released are proportional to the dilution of the sol.

3. The amounts of free ferrocyanide released after the fourth and fifth days of dialysis are the same, and show practically no dilution effect.

From the foregoing observations, it is, therefore, evident that the cobalt ferrocyanide sol. on precipitation shows a marked tendency to hydrolyse. It is further observed that the sol. shows greater variation with temperature and dilution in the undialysed state and their effect becomes less and less, as the dialysis proceeds. It appears that the hydrolysed sols. gradually attain a steady composition after a few days of dialysis, as is shown by the fact that the dilution effect practically becomes negligible after the fourth or fifth day of dialysis.

At this stage it is necessary to recapitulate the observations on the results of conductometric, potentiometric and thermometric titrations of $CoCl_2$ with K_4FeCy_6 described in Part I of this communication. It was observed that the titre values obtained by these three methods in purely aqueous and aqueous-alcoholic solutions showed certain characteristics which had been explained by the possibilities of such phenomenon as (i) hydrolysis and (ii) adsorption, the former influencing the composition of cobalt ferrocyanide to a great extent.

In direct titrations when $CoCl_2$ is added to K_4FeCy_6, the observed titre value for 10.0 c.c. of potassium ferrocyanide decreased from 12.1. c.c., in the aqueous medium, to 11.0 c.c. in aqueous-alcoholic medium, and, in the reverse titrations, when potassium ferrocyanide is added to cobalt-chloride, the observed titre value for 10.0 c.c. of $CoCl_2$ increased from 7.7 c.c. to 9.0 c.c. The fact that the titre values in the aqueous alcoholic medium approach the theoretical value (10 c.c.) goes to prove that the precipitates of cobalt ferrocyanide hydrolyse and that this tendency is checked in non-aqueous medium. Our experiments on the estimations of free ferrocyanide at different dilutions and at different stages of dialysis confirm the views put forward to explain the changeable composition of this complex (vide Part I).

Alongside, with hydrolysis, studies in adsorption have also given important results which show the influence of this phenomenon on the composition of cobalt ferrocyanide. It will be observed that the adsorption isotherm equation $\frac{x}{m} = \alpha \frac{1}{cn}$ is satisfied for the adsorption of K_4FeCy_6 by the precipitated complex (vide Table III, Fig. 3). The shape of the curve for the adsorption of $CoCl_2$ however, is not parabolic, yet it shows that cobalt chloride is also adsorbed by the precipitates (vide Table II; Fig. 2).

On the basis of our experiments on the composition of cobalt ferrocyanide by physico-chemical methods, it was shown that the complex can be represented by the formulae $K_4Co_4Fe(Cy_6)_3$ and $K_2Co_3(FeCy_6)_2$, according as $CoCl_2$ is added to $K_4Fe(CN)_6$ or *vice versa.* These compounds, however, can be formulated as $2Co_2FeCy_6$. K_4FeCy_6 and Co_2FeCy_6. $K_2CoFeCy_6$ respectively. The formation of such compounds can possibly be explained on adsorption of $FeCy_6^{----}$......and Co^{++} and find experimental support by our experiments on adsorption.

PENTAD SYSTEM OF 2—FORMYL KETONES

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AND

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In our previous communications (2, 3, 4, 5) we reported the enol content of 2—formyl ketones. In these ketones two triad systems are superimposed giving rise to a pentad system. The discussion of the equilibria involved in those compounds was long due. On account of unsymmetrical structure 2—formyl ketones (I) can enolise theoretically in two different ways producing the enols (II) and (III) which are structural isomers.

$$\underset{(I)}{R-CO-CH_2-CHO} \qquad \underset{(II)}{R-CO-CH{=}CHOH} \qquad \underset{(III)}{R-C(OH){=}CH-CHO}$$

In an equilibrium mixture all the three forms may co-exist. But on account of their strongly acid character Claisen (6) assigned to them the hydroxymethylene structure (II). The following chemical evidence also points the higher reactivity of form (II).

Joshi, Kaushal and Deshapande (12) had carried out Michael condensation with cyanacetamide and formyl methyl ethylketone. By the formation of 2:3 dimethyl pyridine, through various stages, they established the hydroxymethylene structure for 2-formyl methylethyl ketone.

The extreme readiness with which formyl acetone and formyl acetophenone undergo self condensation to yield 1:3:5 triacetyl benzene and 1:3:5 tribenzoyl benzene respectively (8, 9) supports the hydroxy-methylene structures for the formyl ketones.

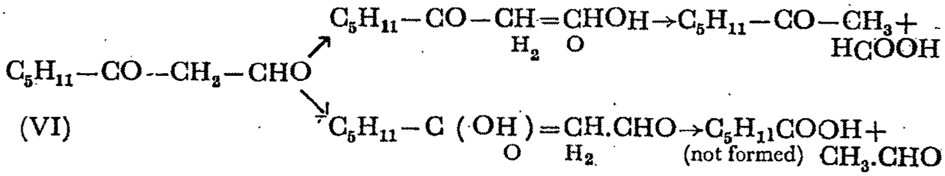
Hydroxylamine hydrochloride acting upon formyl acetone produces 3-methyl-iso-oxazole (7).

The question can however be approached from another side E. H. Ingold[11] has shown that there is close resemblance between aldol condensation and keto-enol (and by analogy aldo-enol) tautomeric change. Both are reversible changes, the only difference in the two being that the former is intermolecular while the later is intra-molecular. Now it is well known that the carbonyl group of an aldehyde is more prone to aldol addition than the carbonyl group of a ketone. Thus in the reversible addition of acetaldehyde to itself the equilibrium is almost completely in favour of acetaldol. In the revesible addition of acetone to itself in aqueous solution Gupta and Deshapande[10] have shown that the equilibrium proportion of diacetone alcohol is only 26%. Further when one molecule of acetaldehyde and one molecule of acetone add reversibly the addition is at the carbonyl group of the aldehyde and not of the ketone.

The product is hydracetyl acetone and not β-hydroxy β-methyl butyric aldehyde.

Since as mentioned above the keto-enol (or aldo-enol) change is parallel to aldol condensation it follows that in a formyl ketone (I) which is a keto-aldehyde the tautomeric change will be at the aldehyde carbonyl rather than at the keto carbonyl group.

In the present investigation it has been observed that formyl methyl n-amyl ketone (VI) on hydrolysis with dilute alkali gave methyl n-amyl ketone and formic acid as the sole products (and no trace of caproic acid and acetaldehyde).

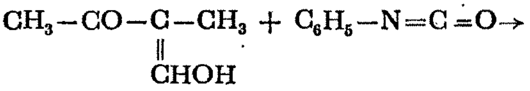


$$C_5H_{11}-CO-CH_2-CHO \nearrow C_5H_{11}-CO-CH{=}CHOH \xrightarrow[H_2\,O]{} C_5H_{11}-CO-CH_3 + HCOOH$$

$$C_5H_{11}-CO-CH_2-CHO \searrow C_5H_{11}-C(OH){=}CH.CHO \xrightarrow[O\;H_2]{} C_5H_{11}COOH + CH_3.CHO$$

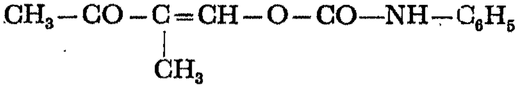
(VI) (not formed)

We further found that formyl methyl ethyl ketone (VII) on being treated with phenyl isocyanate yielded carbanilic acid β methyl β acetyl vinyl ester (VIII) and not ∝β. dimethyl β formyl vinyl ester (IX) as the product did not show any property of aldehyde group.



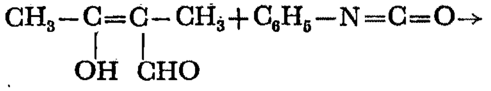
$$CH_3-CO-\underset{\underset{CHOH}{\|}}{C}-CH_3 + C_6H_5-N{=}C{=}O \rightarrow$$

(VII)

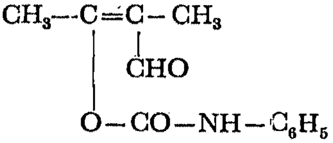


$$CH_3-CO-\underset{\underset{CH_3}{|}}{C}{=}CH-O-CO-NH-C_6H_5$$

(VIII)



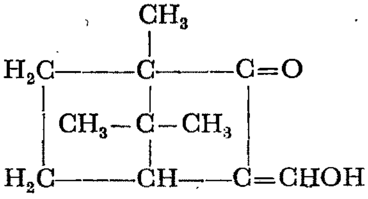
$$CH_3-\underset{\underset{OH}{|}}{C}{=}\underset{\underset{CHO}{|}}{C}-CH_3 + C_6H_5-N{=}C{=}O \rightarrow$$

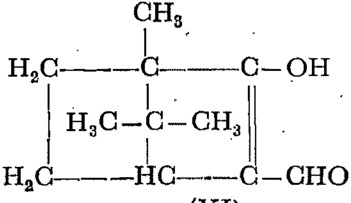


$$CH_3-\underset{\underset{O-CO-NH-C_6H_5}{|}}{C}{=}\underset{\underset{CHO}{|}}{C}-CH_3$$

(IX)

By the oxidation of oxymethylene camphor (X) with chromic acid in acetic acid Bishop, Claisen and Sinclair[1] obtained camphor quinone and with alkaline $KMnO_4$ they obtained camphoric acid. We oxidised it with Kiliani's dichromate mixture[13] and obtained a mixture of camphor quinone and camphoric acid and by limiting the time of contact with the oxidant only camphor quinone was obtained. Formation of camphor quinone cannot be explained by the alternate enol structure of formyl comphor (XI).


(X)


(XI)

However there is evidence for the existence of the form (III) also. For instance with formyl acetone, hydroxylamine not only produces the 3 methyl iso-oxazole but also 5-methyl iso-oxazole in good amount.

Pope and Read[14] studies the mutarotation of the condensation products of oxymethylene camphor with primary and secondary amino compounds and there-by proved the existence of the two enolic forms.

Experimental

Hydrolysis of oxymethylene methyl n-amyl ketone:—Caustic soda solution (15 c. c., 10%) was added to oxymethylene methyl n-amyl ketone (2 g.) in a small R. B. flask fitted with an air condenser and the mixture was gently refluxed on a sand bath for five hours when a reddish oily layer was seen floating over the aqueous alkali. This was extracted with ether. The ethereal extract washed, dried and solvent removed. The residual liquid distilled at 148°C–151°C. Its semicarbazone melted at 119° C and mixed m. p. with a genuine sample of semicarbazone of methyl n-amyl ketone was found to be 119°C.

Form the aqueous alkaline part no acid could be obtained after acidifying and extracting with ether. But on careful neutralisation it gave red colour with ferric chloride solution and a white precipitate mercuric chloride solution, indicating the presence of formic acid.

Treatment of Oxymethylene Methyl Ethyl Ketone with Phenyl Isocyanate:— To a solution of oxymethylene methyl ethyl ketone (4 g.) in dry benzene phenyl isocyanate (4.6 g.) was added and the reactants were warmed for a short time. On cooling a colourless crystalline solid separated. After crystallisation from benzene it melted at 126°C.

It is a colourless, needle shaped crystalline campound. It does not give any colour with ferric chloride. It neither reduces fehlings solution nor does it restore the colour of schiff's reagent. Found N, 6.5, where as $C_{12}H_{13}O_3N$ required N, 6·6 percent.

Oxidation of Oxymethylene Camphor by Kiliani's Dichromate Mixture:— A mixture of oxymethylene camphor (1·8 g.) and Kiliani's dichromate mixture ($K_2Cr_2O_7$ 5·5 g. H_2SO_4 Conc. 3 c.c., H_2O 25 c.c.) was kept at room temperature with occasional shaking for 24 hours. The products of oxidation were repeatedly extracted with ether. The ethereal extract was washed twice with alkali and then with water. After drying over fused calcium-chloride and evaporation the ethereal extract gave a solid substance which on crystallisation melted at 198°C. Its mixed melting point with an authentic sample of camphor quinone was 198°C.

The alkaline part after acidifying and extracting with ether gave a soil product which melted at 187°C on crystallisation. Its equivalent weight was found to be 198·7 (camphoric acid melts at 187° C. and its equivalent weight is 200).

On reducing the time of contact to two hours comphor quinone was found to be the only product of oxidation.

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ON THE FORMATION AND STABILITY OF ACID CARBONATES OF METALS OTHER THAN ALKALI METALS

Part I

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AND

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The acid carbonates of divalent manganese, chromium, iron and cobalt have been isolated for the first time in the solid state. In cases of nickel and silver, the bicarbonate formation takes place to a partial extent only. On the other hand, the trivalent aluminium, chromium, and iron yield only normal carbonates while curpric salts yield a basic carbonate.

Introduction

Keiser and coworkers (J. Amer. Chem. Soc. *30*, 1711, 1908) investigated only the acid carbonates of Calcium and Barium and Haider, Aziz and Langer (J. Ind. Chem. Soc. *21*, 178, 1944) that of Strontium. Later the present author (J. Ind. Chem. Soc. Vol. *25*, No. 10, 1948) succeeded in isolating the acid carbonates of Beryllium, Magnesium, Zinc, Cadmium, and Mercury (-i c). In order to advance the study of these compounds an attempt has now been made to investigate the conditions of formation and stability with respect to the bicarbonates of divalent Manganese, Chromium, Iron, Cobalt, Nickel andCopper ; trivalent Aluminium, Chromium and Iron and univalent Silver.

Experimental

The bicarbonates of these metals were, therefore, prepared by mixing solutions of $KHCO_3$ with the corresponding soluble salts of the metals all cooled to O°C. However, in the cases of Cr^{++}, Cu^{++}, Al^{+++}, Cr^{+++}, and Fe^{+++}, salts the solutions had to be neutralised before prepitation. The precipitates were washed successively with ice cold water (saturated with CO_2), alcohol and ether and dried at O°C.

A. The decomposition temperature of each of these precipitates was found by gradually raising the temperature of the ice cold water bath inside which the boiling tube containing the precipitate was placed. The decomposition temperature was recorded when the CO_2 evolved from the precipitate on passage through a little lime water just turned the latter turbid.

Table No. 1

No.	Name of Bicarbonate of metal	Decomp. Temp. without gelatine	Decomp. Temp. with O. 5% gelatine	Decomp. Temp. with 2 % gelatine	Decomp. Temp. with neutral soln of silica-gel.
(1)	Mn^{++}	4°C	6°C	8°C	8°C
(2)	Cr^{++}	9°C	11°C	13°C	13°C
(3)	Fe^{++}	16°C	18°C	20°C	20°C
(4)	Co^{++}	9°C	11°C	13°C	13°C
(5)	Ni^{++}	5°C	7°C	8°C	8°C
(6)	Cu^{++}	18°C	20°C	22°C	22°C
(7)	Al^{+++}	4°C	6°C	8°C	8°C
(8)	Cr^{+++}	9°C	11°C	13°C	13°C
(9)	Fe^{+++}	3°C	5°C	10°C	10°C
(10)	Ag^{+}	16°C	18°C	20°C	20°C

The results in the above table lead us to the conclusion that the decomposition temperatures of the bicarbonates of metals under consideration are raised by :—

(a) The presence of gelatine.
(b) Increasing concentration of gelatine.
(c) The presence of a neutral solution of silica gel.

B. The ratio of CO_2 to the oxide in these precipitates war determined by the method of Keiser and Mac. Master (J. Amer. Chem. Soc. *30*, 1715, 1908) as improved by Haider et. al. and later by the present author (jour. Ind. Chem. Soc. Vol. *25*, No. 10, 1948).

PROCEDURE

The precipitate of the prepared bicarbonate was introduced in the flask where it was decomposed by addition of acid and subsequent heating. The weight of CO_2 was determined by absorbing it in weighed sofnolite tubes, and that of the oxide was determined in the remaining solution in the flask after filtering and estimating it by the usual gravimetric methods.

Thus, by getting the ratio of CO_2 to that of oxide in all these cases, the formulae of the parent bicarbonates were arrived at, the ratio of the molecules was calculated in the following way:—

$$\frac{\text{Wt. of Oxide}}{\text{Mol. Wt. of Oide}} = \frac{\text{Wt. of } CO_2}{\text{Mol. Wt. of } CO_2}$$

For example, substituting the values for Manganese Bicarbonate, the value of X, i.e. the mean $\frac{CO_2}{\text{Oxide}}$ ratio can be calculated as :—

M_nO : CO_2

$\frac{0.1480}{71.0}$: $\frac{0.2040}{44}$ gm. mols.

0.00208 : 0.00463 gm. mols.

Simplest Ratio 1 : 2.22

The following table indicates the nature of results obtained:—

Table No. II

No.	Name of Bicarbonate of Metal	Mean $\frac{CO_2}{\text{Oxide}}$	Formula
(1)	Mn^{++}	2.20	$Mn(HCO_3)_2\ 0.20\ CO_2$
(2)	Cr^{++}	2.16	$Cr(HCO_3)_2\ 0.16\ CO_2$
(3)	Fe^{++}	2.26	$Fe(HCO_3)_2\ 0.26\ CO_2$
(4)	Co^{++}	2.02	$Co(HCO_3)_2\ 0.02\ CO_2$
(5)	Ni^{++}	1.32	$Ni(HCO_3)_2\ 2\ NiCO_3$
(6)	Cu^{++}	0.63	$5\ CuO.\quad 3\ CO_2$
(7)	Al^{+++}	3.11	$Al_2(CO_3)_3\ 0.11\ H_2CO_3$
(8)	Cr^{+++}	3.09	$Cr_2(CO_3)_3\ 0.09\ H_2CO_3$
(9)	Fe^{+++}	3.01	$Fe_2(CO_3)_3\ 0.01\ H_2CO_3$
(10)	Ag^{+}	1.20	$Ag_2CO_3.\ 0.2\ AgHCO_3$

The above results establish the existence of the bicarbonates of divalent cations like Manganese, Chromium, Iron and Cobalt. In cases of trivalent Aluminium. Chromium, and Iron the double decomposition method yields only the normal carbonates. In the case of Nickel and Silver the bicarbonate formation takes place to a partial extent only while cupric salts apparently yield a basic carbonate.

Experiments on the detection of carbonate and bicarbonate redicals showed that the best way of distinguishing between the carbonate and bicarbonate radicals is as follows:—

To the precipitate to be tested for bicarbonate, add a little water, then, a little bleaching powder, KBr and chloroform and shake. If bicarbonate is present, bromine is liberated which gives a yellow or brown colour in the layer of chloroform. (In the case of insoluble bicarbonates a little sodium carbonate should be added to release the more soluble sodium bicarbonate formed by double decomposition).

ACKNOWLEDGMENT

The author's thanks are due to Dr. R.C. Mehrotra, D. Phil. Alld., Ph.D. London, Reader in Chemistry for his help and Dr. A. C. Chatterji, D. Sc., Head of the Deptt. of Chemistry, Lucknow University, Lucknow for the grant of Laboratory facilities.

PARACHOR AND HYDROGEN BONDING

Part I—NITRO COMPOUNDS AND ALCOHOLS

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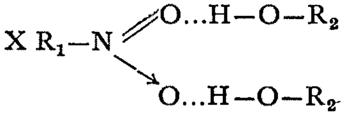
Chemistry Laboratory, Holkar College, Indore.

In a number of papers published from this laboratory by Bhagwat and co-workers (3,4) it has been shown that association between different molecules by hydrogen bonding causes a parachor drop of 8-10 units.

Baker (2) and Pauling (9) have shown that there are a number of compounds, notably 2,6-dihydroxy benzoic acid, 1, 8 dihydroxy anthraquinone, 2, 2' dihydroxy benzophenone there are two internally compensated hydrogen bonds. Since the electronegativity of the oxygen atom in the carboxyl group is divided between the two hydrogen atoms the bond formed is a weak bond. Pauling has mentioned the possibility of a similar bond formation in the nitro compounds with two hydroxyl groups in the adjoining positions, as in compounds like 2-nitro resorcinol. In such cases the bond is a strong bond because one oxygen atom is independently available for its formation. In these and the above-mentioned cases the bond is entirely internally compensated. We have, in this paper, tried to prove that due to the strongly electronegative character of the nitro group it will form molecular compounds with alcohols in which two molecules of alcohols are linked to the nitro group by hydrogen bonds forming the compound



$$X\,R_1{-}N\begin{matrix}\nearrow O\ldots H{-}O{-}R_2\\ \searrow O\ldots H{-}O{-}R_2\end{matrix}$$

The procedure adopted consists in finding out the parachors of the nitro compounds and the alcohols separately and then of the nitro compounds in solution in alcohols. The values obtained in solution are then compared with the observed values of the pure liquids. This method balances any error due to slight impurity or any personal error. It may involve a slight deviation from the absolute values but the net conclusions remain unaffected.

Table I

Parachor of nitro compounds and alcohols

Substance	temp °C	Density	Surface Tension	Parachor
Methyl alcohol	21.5	0.7954	22.02	87.4
Ethyl alcohol	21.5	0.8039	21.72	124.0
Amyl alcohol	23.0	0.8117	24.32	241.8
Nitrobenzene	23.0	1.2070	44.70	263.6
O-nitrotoluene	22.0	1.1639	41.79	299.3
p-chloroniline				273.9 (calculated value)

Table II

x =molar fraction of the solute.
r =surface tension of the solution
d =density of the solution M_m=mean molecular weight
P_m=observed parachor of the mixture
P_x=observed parachor of the solute in solution

Parachor of Nitro-benzene in alcohols

x	M_m	T°C	d	r	P_m	P_x
Solvent—*Methyl alcohol*						
0.2005	50.29	20	0.9650	26.73	118.8	244.1
0.4039	68.81	20	1.0712	30.54	151.3	245.6
0.5988	86.52	20	1.1320	32.47	182.8	246.7
0.7886	103.84	20	1.1735	33.11	212.6	246.2
0.8030	105.10	20	1.1747	34.10	216.5	248.2
0.8990	113.90	20	1.1908	36.95	236.2	252.9
Solvent—*Ethyl alcohol*						
0.2787	66.54	20	0.9730	27.47	156.9	242.2
0.4658	81.94	20	1.0521	27.86	179.3	243.0
0.5400	87.65	20	1.0791	28.77	188.5	243.4
0.6798	98.43	20	1.1237	29.67	204.8	242.9
0.8084	108.32	20	1.1602	33.38	224.3	249.3
0.8767	113.60	20	1.1750	35.94	237.2	253.1
Solvent—*Amyl Alcohol.*						
0.1799	94.44	23	0.8714	25.01	243.0	249.1
0.4895	105.20	23	0.9988	27.77	242.4	243.1
0.5464	107.23	23	1.0210	28.46	243.1	244.3
0.7865	115.60	23	1.1180	30.28	243.2	243.5
0.8502	117.90	23	1.1400	31.40	244.8	245.4
0.8730	118.60	23	1.1570	32.28	244.4	244.7
0.9221	120.30	23	1.1670	35.15	251.6	252.5

Table III

PARACHOR OF O-NITRO TOLUENE IN DIFFERENT SOLVENTS.

Solvent—*Methyl Alcohol.*

x	M_m	T °C	d	r	P_m	P_x
0.1362	46.33	20.0	0.9170	25.39	113.6	279.8
0.2963	63.15	20.5	1.0053	27.77	144.5	280.2
0.4290	77.11	21.5	1.0637	29.26	170.7	281.5
0.6195	97.12	20.0	1.1044	30.78	207.6	281.5

Solvent—*Ethyl Alcohol.*

x	M_m	T °C	d	r	P_m	P_x
0.1922	63.56	22.0	0.9255	25.14	154.2	280.9
0.2604	69.79	23.0	0.9577	26.26	165.4	282.9
0.4451	87.49	22.3	1.0283	27.65	195.6	281.3
0.5077	92.19	22.0	1.0506	29.26	204.6	282.8

Solvent——*Amyl Alcohol*

x	M_m	T °C	d	r	P_m	P_x
0.2909	102.30	21.3	0.9221	26.46	252.2	277.7
0.3481	105.20	21.0	.2434	27.11	254.9	279.6
0.4219	108.80	21.5	0.9692	27.20	256.9	278.1
0.5001	112.64	22.0	0.9958	27.61	259.8	278.4
0.5971	117.38	21.0	1.0304	28.86	264.7	279.8

Table IV

PARACHOR OF P-CHLORO-ANILINE IN DIFFERENT SOLVENTS.

Solvent——*Methyl Alcohol.*

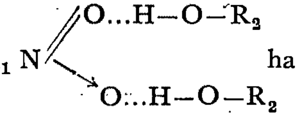
x	Mm	To c	d	r	Pm	Px
0.0613	37.84	22	0.8630	24.75	08.04	261.0
0.0980	41.38	21	0.9001	26.41	104.40	260.0

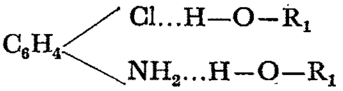
Solvent——*Ethyl Alcohol*

X	M_m	°C	d	r	P_m	P_x
0.0870	52.20	20	0.8732	24.38	135.6	258.0

Solvent——*Amyl Alcohol.*

X	M_m	T°C	d	r	P_m	P_x
0.0842	91.46	22.0	0.8416	24.77	243.0	256.5
0.1334	93.60	21.0	0.3705	26.36	244.1	258.6
0.1887	95.24	22.0	0.8880	26.65	244.2	255.2
0.1936	95.75	32.5	0.8874	26.02	244.8	265.3

Since the H-bond is responsible for a drop of 8-10 units in parachor two such bonds will cause a decrease of 16-20 units. The drop is to some extent dependant upon the strength of the bond and probably on the number of molecules associated. Our results show a drop of 18 units in the case of nitro-benzene and o-nitro-toluene. The values for pure liquids are 263.6 and 299.3 respectively while in solution in various alcohols they are about 243 and 281. It is worth while to note that all these alcohols are associating liquids. This means that the compound of the type  $R_1N\left<\begin{array}{l}O\ldots H-O-R_2\\ O\ldots H-O-R_2\end{array}\right.$ has been formed.

The other compound studied to bring about the quantitative nature of parachor in establishing H-bonds in p-chloraniline where Cl and NH_2 being negative are capable of forming H-bonds and therefore a similar drop should be obtained. The calculated parachor of p-chloraniline is 273.9 and its values are 261, 258,257 in methyl, ethyl and amlyl alcohols respectively. Although the decrease in methyl alcohol is lower it may be due to low molar fraction and the volatile nature of the solution. In other alcohols the drop is of about 16 units showing that the compounds of the type  $C_6H_4\left<\begin{array}{l}Cl\ldots H-O-R_1\\ NH_2\ldots H-O-R_1\end{array}\right.$ are formed. Another phenomenon worth noting is that upto the molar fraction of 0.9 there is scarcely any change in parachor with concentration, which is not in concurrence with the observation of Hammick and Andrew (6) that the prachor changes with concentration when the difference of the surface tensions of the solvent and the solute is about 14 units. When the molar fraction is 0.9 or greater there is a slight increase in the value probably owing to the fact that the solvent molecules are too few for the formation of the hydrogen bond.

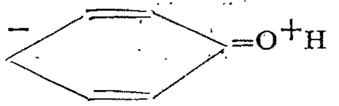
Simultaneous to this the parachor of the nitro compounds was also determined when dissolved in phenol.

Table IV

Parachor of the nitro compounds in phenol

x	M_m	T °C	d	r	P_m	P_x
Solute—*Nitrobenzene*						
0.3379	103.0	22	0.1230	43.64	238.3	264.5
0.4906	108.3	22	1.1430	43.39	243.7	263.1
0.5433	109.8	22	1.1530	43.94	245.8	263.2
0.7904	117.0	21	1.1790	43.86	255.7	263.7
0.8944	119.2	20	1.1930	43.98	257.8	261.6
Solute—*o-nitrotoluene*						
0.3145	107.7	21	1.1101	43.01	249.1	301.4
0.4073	111.6	22	1.1182	42.69	255.8	300.6
0.6227	120.9	21	1.1358	42.27	272.0	300.4
0.6538	122.2	22	1.1392	42.62	274.8	301.2

Thus when phenol is used as a solvent there is no drop in parachor in the case of the two nitro compounds studied, showing that no hydrogen bonds have been formed. This behaviour of the nitro compounds and the phenol is very interesting taking into consideration the fact that both groups are strongly electronegative . Pauling (7) has stated that the phenols form hydrogen bonds stronger than the aliphatic alochols because of the increase in the electronegativity of the oxygen atom resulting from resonance with structure such as:



This statement and another due to Pauling (8) that a phenolic hydroxylic group forms a strong hydrogen bond with an oxygen atom of an adjacent nitro group due to structural proximity and our finding that the alcohols are forming strong hydrogen bonds with the nitro group while the phenol does not form any, is, contrary to it. For comparison two phenols and an aromatic alcohol were taken as solvents for nitrobenzene. The results are:—

Table V

Parachor of nitrobenzine

Solvent	x	t	d	r	P_m	P_x
0-oresol	0.1552	40	1.056	38.45	257.6	259.6
benzyl alcohol	0.3766	30	1.099	40.42	260.6	262.6
thymol	0.7710	20	1.177	38.70	282.6	263.0

These figures also show that there is, as in the case of phenol, no hydrogen bond formed between the nitro-group and the hydroxyl group.

Badger and Bauer (1) suggest that the hydrogen bond formation is affected by steric hindrances. The parachor of nitrobenzene calculated from the results obtained by Deshapande, Kaveeshwar and Bhagwat (5) for nitrobenzene and menthol mixture give a value of 247.5 for nitrobenzene showing that menthol with as large a cross-sectional area as phenol does form a compound of the type mentioned above while phenol does not. Kaveeshwar (Thesis submitted for the Ph.D.) suggests that this peculiar phenomenon may find an explanation in that the solvent-solute hydrogen bond formation may possibly be affected by their surface tension difference and that it may be formed when these differ by more than 10 units.

Thus it is possible to use parachor, may be with some limitations, as a valuable tool for estimation of the number and the bond strength of the hydrogen bond.

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PARACHOR AND HYDROGEN BONDING

Part II—Effect of Surface Tension

By V.M. Bhale, S.N. Kaveeshwar, and H.K. Sharma,
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In a paper previous to this[1] it is shown that parachor can be utilised as an instrument not only for detection but also to find the number and possibly the strength of the hydrogen bonds. It is not possible for any indirect method to do this. It was further mentioned, while considering the non-formation of the hydrogen bond between the nitro compounds and the phenol, that the hydrogen bond formation may possibly be affected by the difference of surface tensions of the solvent and the solute. In the present paper we have attempted to investigate further into the phenomenon.

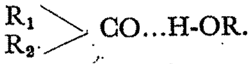
Lowry and Bennett (2) suggested molecular association between ketones and alcohols. It is obvious that this link will be through a hydrogen bond forming a compound of the type  $\begin{matrix}R_1\\R_2\end{matrix}\!\!>CO...H\text{-}OR$. To study the effect of surface tension we have selected eight pairs of ketones and alohols where the difference of surface tension between the solvent and the solute is below 5 units, and about 14 units in other pairs. The procedure consists in finding out the parachor of the pure ketones and the alcohols and then the ketones in alcohols. This method balances any errors due to impurity or due to personal error and may involve some deviations from the absolute values but the net conclusions remain unaffected.

Table I

Substance	temp° C	Density	Surface tension	Parachor
methyl alcohol	19	0.7992	22.00	87.5
ethyl alcohol	21	0.7915	21.78	125.5
benzyl alcohol	19	1.0449	42.48	264.0
cinnamyl alcohol	45	1.0340	40.28	326.5
acetone	21	0.8015	23.90	160.0
ethyl methyl ketone	22	0.8007	25.00	201.1
acetophenone	21	1.0246	38.91	292.4
benzophenone	—	—	—	428.2 (Calculated)

Table II

x = molar fraction of the solute d = density of the solution.
M_m = mean molecular weight of the solution
r = surface tension of the solution
P_m = parachor of the solution P_x = parachor of the solute

Parachor of acetone in various solvents

x	M_m	t°C	d	r	P_m	Px
Solvent-methyl alcohol						
0.1802	36.68	21	0.7912	22.22	100.7	161.0
0.2204	37.73	20	0.7921	22.49	103.7	160.7
0.2466	38.41	19	0.7932	22.89	105.9	162.2
0.3674	41.54	22	0.7947	23.44	115.0	162.3
Solvent-ethyl alcohol						
0.3890	50.52	21	0.7831	21.82	139.4	161.5
0.4315	51.17	22	0.7824	22.08	141.8	163.3
0.4798	51.76	21	0.7812	21.52	142.7	161.9
0.5001	52.05	21	0.7800	21.40	143.5	161.6
Solvent--benzyl alcohol						
0.2493	93.24	22	1.0020	37.73	230.7	151.2
0.3427	90.86	20	0.9946	36.84	225.5	151.7
0.4234	87.85	21	0.9847	35.54	217.8	154.6
0.5107	82.46	21	0.9607	34.86	208.5	155.3
Solvent—cinnamyl alcohol						
0.4677	98.44	35	0.9639	32.88	244.3	150.8
0.5534	91.93	31	0.9540	32.69	230.5	152.9
0.6301	86.09	35	0.9444	32.01	215.3	150.0
0.6963	81.07	35	0.9335	31.80	206.2	153.7
Parachor of ethyl methyl ketone in various solvents						
Solvent-methyl alcohol						
0.2518	42.09	23	0.8016	23.72	116.6	203.0
0.3976	47.92	22	0.8021	25.14	133.8	203.9
0.4257	50.11	23	0.8080	26.61	140.9	205.1
0.5178	52.77	23	0.8092	25.80	147.0	202.3
Solvent—ethyl alcohol						
0.2500	51.63	21	0.7907	24.28	144.9	202.4
0.3486	55.31	22	0.8022	24.45	153.3	203.2
0.4176	56.89	22	0.8042	26.00	159.8	207.5
0.4315	57.25	20	0.8048	25.14	159.3	204.0

x	M_m	t° C	d	r	P_m	Px
Solvent-benzyl alcohol						
0.4698	91.16	21	0.9530	34.70	229.7	190.9
0.4819	90.69	21	0.9512	34.01	230.2	193.6
0.5209	89.30	21	0.9492	33.86	227.0	192.8
0.5469	88.32	21	0.9476	33.64	224.5	191.8
Solvent-Cinnamyl alcohol						
0.4335	107.1	34	0.9584	33.51	268.7	193.2
0.4945	103.3	34	0.9646	32.80	258.8	190.1
0.5917	97.37	32	0.9404	32.34	246.9	191.8
0.6637	92.84	35	0.9301	32.02	237.5	192.1
Parachor of acetophenone in various solvents *Solvent--methyl alcohol*						
0.1825	47.06	22	0.9136	32.36	123.4	284.2
0.2768	56.38	22	0.9576	34.01	142.2	285.0
0.2841	57.00	22	0.9612	34.81	143.9	286.0
0.4303	69.86	22	0.9812	35.10	173.0	285.8
Solvent - ethyl alcohol						
0.2826	66.91	23	0.9120	28.25	169.3	280.1
0.3158	69.37	22	0.9162	28.50	174.9	281.2
0.3452	71.56	22	0.9212	28.77	179.9	283.0
0.4034	75.87	21	0.9402	31.40	191.0	287.7
Solvent- benzyl alcohol						
0.3238	111.9	21	0.0284	40.20	274.0	295.2
0.4562	113.5	21	1.0342	41.88	279.3	297.4
0.4750	113.8	21	1.0410	42.27	278.5	294.5
0.5486	114.6	22	1.0432	42.81	281.1	295.2
Solvent - cinnamyl alcohol						
0.3733	128.8	35	1.0264	39.19	314.2	293.7
0.4192	128.1	35	1.0300	39.98	312.7	293.6
0.5177	126.8	35	1.0255	38.60	308.4	291.7
0.6284	125.2	35	1.0204	38.41	305.6	293.2

x	M_m	t°C	d	r	P_m	P
Parachor of benzophenone in various solvents						
Solvent-methyl alcohol						
0.0508	39.6	21	0.8496	24.88	104.2	415.9
0.0664	41.9	21	0.8600	25.17	109.2	414.5
0.0976	45.7	21	0.8851	27.19	118.0	420.0
0.1069	47.9	21	0.8921	27.84	123.1	420.6
Solvent-ethyl alcohol						
0.1012	59.7	21	0.8552	24.64	155.2	418.4
0.1043	60.2	22	0.8582	24.86	156.1	418.9
0.1319	64.0	22	0.8814	26.00	163.9	416.2
0.1536	66.9	22	0.8901	26.86	171.1	421.5
Solvent-benzyl alcohol						
0.1266	117.4	21	1.0573	44.38	286.4	430.4
0.1866	121.3	22	1.0652	45.45	295.0	432.2
0.1932	122.3	21	1.0644	43.73	296.2	431.0
0.1992	122.7	22	1.0661	44.63	297.4	432.1
Solvent-cinnamyl alcohol						
0.1074	139.2	35	1.0506	43.42	340.2	429.5
0.1751	142.4	34	1.0630	44.11	344.9	431.2

The methyl and ethyl alcohols and the two ketones, acetone and methyl-ethyl ketone, have surface tensions between 21 and 25 while benzyl and cinnamyl alcohols and acetophenone and benzophenone have surface tensions between 38 and 42 units. From these alcohol-ketone pairs have been chosen such that their solvent-solute surface tension difference is either below 5 or about 14.From the above tables we find that acetone and methyl ethyl ketone show no hydrogen bond formation when dissolved in methyl and ethyl alcohols and their values are about 161 and 203 respectively very near to their parachor in pure condition viz. 160.0 and 201.1. But when they are dissolved in benzyl and cinnamyl alcohols the values are about 152 and 192 showing a drop of 8-10 units. A similar observation was made in the case of acetophenone and benzophenone and they registered no fall in parachor when dissolved in benzyl and cinnamyl alcohols—solvents which have nearly the same surface tension—and the parachors in solution are 295 amd 430 quite near those in pure condition. But when the same ketones are dissolved in methyl and ethyl alcohols the values become 284 and 418 respectively showing a hydrogen bond formaton.

This clearly shows that the solvent-solute hydrogen bond is affected by their surface tensions difference; and apart from the ordinary condition of having two negative groups for the formation of a hydrogen bond of a solvent-solute type it also seems necessary to have a difference of about 14 units in their surface enstions.

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1. BHAGWAT, KAVEESHWAR and DWIVEDI. This J. p.
2. LOWRY and BENNETT. 1929., J. Chem. Soc. 256.

STUDIES IN THE CO-ORDINATION COMPOUND OF CARBONDISULPHIDE BY PARACHOR

By R. P. SHUKLA and C. S. BHANDARI, *Department of Chemistry,*
Holkar College, Indore.

When the liquids of similar polarity and chemical structure are mixed there is generally little change in volume, only small change in Roult's law and very little heat of solution. This behaviour occurs on mixing methyl and ethyl alcohol etc. If, however, the substances interact strongly as occurs, for example, in acetone and chlroform where hydrogen-bonding occurs thereis generally observed a decrease in volume, a lowering in vapour pressure compared with that predicated by Roult's law and a positive heat of solution. Sometimes, on mixing a polar liquid and a nonpolar liquid the reversees effect is observed and there is an increase in volume, increase in the vapour pressure and a positive heat of solution. Thus when CS_2 is mixed with acetone the volume is increased by 1.4% Similarly the heat of solution and the vapour pressure are increased by 5.0% and 3.1% respectively. These results will be due to the energy of interaction of the unlike molecules being greater than the sum of the energies of interaction of like molecules.

In the present work it has been proposed to see if parachor can also show the interaction or co-ordination of unlike molecules in the last case, that is, CS_2 and acetone.

EXPERIMENTAL

MIXTURE OF CARBONDISULPHIDE IN ACETONE

Table No. 1

$x=0.3506$ $M_m=0.6494$ $1-x$ 0.6494.

T^oC	'd'	'r'	P_m	P_x
23.2	0.92929	17.765	142.04	106.10
30.8	0.91938	18.138	144.28	112.46
35.9	0.91201	17.696	144.61	113.40

Table No. 2

$x=0.51143$ $M_m=67.202$ $1-x$ 0.48857

T in°C	'd'	'r'	P_m	P_y
23.2	0.9922	20.277	143.68	126.65
30.0	0.9831	17.758	140.26	119.98
33.6	0.97747	19.925	145.15	129.41

Table No. 3

21

$x=0.44126$ $M_m=65.940$ $1-x$ 0.5587

T°C	'd'	'r'	P_m	P_x
21.3	0.96118	24.677	152.90	142.01
23.3	0.95852	20.830	146.92	128.47
30.2	0.94994	21.607	149.650	134.65

Table No. 4

$x=0.73367$ $M_m=71.202$ $1-x$ 0.26633

T°C	'd'	'r'	P_m	P_x
21.2	1.1066	18.647	133.69	123.62
23.5	1.1035	23.801	142.46	135.55
31.4	1.0919	23.410	140.25	132.5

Table No. 5

$x=0.77254$ $M_m=69.574$ $1-x$ 0.3572

T°C	'd'	'r'	Pm	P_x
19.2	1.1319	23.54	139.93	153.60
23.8	1.1257	24.513	142.11	136.46
31.0	23.753	23.752	142.21	135.42

Table No. 6

x=0.6433 M_m=69.574 1—x 0.3672

T°C	‘d’	‘r	Pm	P_x
10.2	1.0595	23.933	145.21	136.71
24.0	1.0544	22.209	144.35	134.30
33.0	1.0406	18.582	138.81	125124

TABLE ‘A’

MOLECULAR COMPOUND

Wt. of CS_2	wt. of Acetone	Temp.°C	‘r’	‘d’	P
15.366	11.4330	23.5	19.970	0.98788	285.60
17.1834	12.1932	23.5	19.697	0.98198	287.42
18.482	14.3716	23.5	19.548	0.98380	286.30
11.7818	8.6716	23.7	19.742	0.98628	286.30
7.7530	5.7726	23.5	19.275	0.98878	283.90
					Average=285.8

DISCUSSION

From various papers published from this laboratory it will be seen that the effect of co-ordination is to reduce the parachor value. Similarly the mixture law of Hammic and Andrews[2] also fails when such co-ordination takes place between the solvent and solute. This is due to the various concentration of the co-ordination compound and the excesses of solvent which are both varying. It will be seen from the results that in the present case also the mixture law fails and we get a value for CS_2 which is always lower than the parachor of pure CS_2 and hence the co-ordination of the two may be inferred. Further the two liquids were mixed in the ratio of their molecular weight and their parachor was determined thinking them to be a single compound. It will be seen from the table ‘A’ that the average parachor value of such a molecular compound comes to be 285,8 while the sum of the parachor of the two (Acetone and CS_2) is 306.4 and thus there is a lowering of 20.6 units, and hence the co-ordination of the two must be inferred, hence the effect is equivalent to two cordination bonds.

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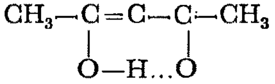
2. SYRKIN and DYATKINA. The structure of Molecule and Chemical Bond, Butterworth Scientific Publications, 1950, pp. 278.
3. Hammic and Andrew's, (1929) J. Chem. Soc. pp. 754.

THE STRUCTURE OF ACETYL ACETONE FROM THE STUDY OF PARACHOR

By S. G. KHANDEKAR, W. V. BHAGWAT and S. N. KAVEESHWAR,
Chemistry Department, Holkar College, Indore.

Pauling (4) has mentioned the formation of hydrogen bond in acetyl acetone, between the hydroxyl group and the adjacent oxygen atom of the Ketonic group. The structure of acetyl acetone according to Pauling is as follows.



$$\begin{array}{c} CH_3-\underset{\displaystyle O-H\ldots}{\overset{}{C}}=C-\underset{\displaystyle O}{C}-CH_3 \end{array}$$

Bhagwat, Shukla and Khandekar (1) have shown that in case of a hydrogen bond there is a sudden fall in the parachor value of about 10 units. It is therefore expected that the parachor value of acetyl acetone should also show a similar decrease. With this object in view the parachor of acetyl acetone in different solvents was studied.

In calculating the parachor of the solute in solution the mixture law of Hammick and Andrew (2) has been used. Surface tension is determined by Jaeger's method. The parachor values in solution are compared with the observed value for the pure liquid to eliminate all personal errors or those due to the presence of slight impurities. Our results are as follows.

Parachor of Acetyl Acetone

Parachor of Acetyl acetone in different solvents. x, molar fraction of Acetyl acetone ; (1-x) molar fraction of the solvent ; r, surface tension of the solution ; d, the density of the solution. Mm mean molar weight ; Pm observed parachor of the mixture ; Px calculated parachor of the acetyl acetone from the solution.

Solvent	*x*	*Mm*	*t°C*	*d*	*r*	*Pm*	*Px*
Benzene	.7281	94.10	39	.8851	23.68	234.55	245.2
	.7467	94.51	31	.8892	24.07	235.44	245.2
	.7656	94.93	34	.8919	24.36	236.50	245.7
	.7938	95.55	34	.8969	24.51	237.09	245.1
Chloroform	.2061	115.42	30	1.340	26.69	195.88	245.4
	.2816	113.95	30	1.322	29.32	200.63	245.9
	.2845	113.90	35	1.289	26.67	200.78	245.6
	.3268	113.08	30	1.276	27.77	203.55	345.3
Carbon tetra Cloride	.2506	140.38	30	1.416	26.98	226.02	245.8
	.3155	136.87	30	1.371	27.11	227.92	245.7
	.3628	134.32	30	1.342	27.39	228.99	245.8
	.4110	131.72	30	1.309	27.45	230.21	245.4
Toluene	.2267	93.44	30	.8809	27.90	245.13	245.3
	.3123	94.60	30	.8900	28.39	245.36	246.2
	.3398	94.82	30	.8923	28.36	245.21	245.7
	.4014	95.30	30	.8982	28.55	245.19	245.4

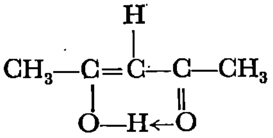
	x	*Mm*	*t°c*	*d*	*r*	*Pm*	*Px*
Dioxane	.2067	90.51	30	1.008	32.54	214.41	246.2
	.2452	90.99	30	1·006	32.18	215.60	245.0
	.3106	91.76	30	1.000	31.80	217.90	244.5
	.3456	92.18	30	.9977	31.80	219.45	244.9
Methyl—Acetate	.2284	78.44	30	.8385	25.13	209.50	245.5
	.2679	79.47	35	.8422	24.47	210.98	244.9
	.3183	80.92	30	.8557	26.04	213.61	245.4
	.3600	82.10	30	.8656	26.60	215.44	244.8

The calculated value of parachor of acetyl acetone is 247.2 and the observed value in solution is about 245.5. Thus there is a decrease of about two units instead of the expected decrease of about 10 units, due to the formation of a hydrogen bond. Sugden (5) has also observed the value of parachor for pure liquid as 245.4. Thus the observed values for parachor of aceetyl acetone whether in pure liquid state or in solution do not suggest the existence of a hydrogen bond as suggested by Pauling.

Pauling (3) has made a mention of a possibility of a second coordinate bond for hydrogen when the bond becomes largely ionic causing an appreciable attraction of L electron and under this circumstance the proton could use its *s* orbital for the coordinate bond formation. It is thus possible for a hydrogen bond to be converted into a coordinate bond.

Hydrogen atom of the hydroxyl group of acetyl acetone is known to be eonic in character being replaceable by metals, resulting in compounds forming a chelate bond. It is possible that this largely ionic character of the hydrogen atom is responsible for the formation of a coordinate bond instead of a hydrogen bond.

Our results for parachor of Acetyl Acetone in both the pure and dissolved state indicate the presence of a coordinate bond. The presense of a covalent bond is indicated by a drop of 1.6 units in the parachor value. Our observed values show a drop of about two units, which corresponds with the formation of a coordinate bond, assuming that the parachor value of ring formation due to a coordinate bond is zero, as in the case of ring formation due to hydrogen bond. It may therefore be concluded that there is a coordinate bond in Acetyl Acetone. Therefore the structure of Acetyl Acetone should be as follows.



$$\begin{array}{ccccccccc} & & & & H & & & & \\ & & & & | & & & & \\ CH_3 & - & C & = & C & - & C & - & CH_3 \\ & & | & & & & \| & & \\ & & O & - & H & \leftarrow & O & & \end{array}$$

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1. Bhagwat W. V., Shukla R. P. and Khandekar S. G. 1952. J. INDIAN. Chem. Soc. page **679**.
2. Hammick and Andrew. 1929. J. Chem. Soc. page **754**.
3. Pauling, "The Nature Of The Chemical Bond." page **284**, foot note.
4. Pauling, "The Nature Of The Chemical Bond." page **318**.
5. Sugden. 1929. J. Chem. Soc. page **316**.

ENTOMOLOGICAL SURVEY OF HIMALAYA*

Part XXI.—Notes on some Coleoptera Collected by Prof. M.S. Mani's Entomological Expeditions to North-West Himalaya.

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This paper deals with a report on part of the coleoptera collected by Prof. M.S.Mani's two Entomological Expeditions to North-West Himalaya during 1954-1955. Some specimens collected earlier from the extreme Western Himalaya are also included. Twenty species are dealt with here. Some of the species are being recorded for the first time from the region.

I thank Prof. M. S. Mani for facilities for work and guidance.

Family CETONIIDAE

Protaetia hieroglyphica (Menetr.)

1832. *Cetonia hieroglyphica, Menetr., Cat. raisonne,* p. 189
1910. *Protaetia hieroglyphica,* Arrow in *Fauna Brit. India,* Coleop. Lamellicornia (Cetoniinae & Dynastinae), p. 159

One male from Narkanda-Kulu Road, 9,000 ft., Coll. H. N. Baijal, 5. x. 1954. This is the first record of this species the east of the Sutlej Valley. It is so far known from Murree, Dehra Ghazi Khan, Turkestan, and Caspian Sea.

Protaetia neglecta (Hope)

1831. *Cetonia neglecta,* Hope, *Gray's Zool. Miscellany,* p. 24.
1910. *Protaetia neglecta,* Arrow in *Fauna Brit. India,* Coleop. Lamellicornia (Cetoniinae & Dynastinae), p. 160

2 males and 4 females, coll. No. 576. 1/55-576.6/55, from Manali, 6500 ft., Coll. Santokh Singh, 25, vi. 1955; 1 female Coll. No. 590. 5/55 from Dalhousie, 7000 ft., Coll. Santokh Singh, 29, vi. 1955; 1 male from Dalhousie, 7500 ft., Coll. M. S. Mani, 22.vi. 1953. This is the first record of the species to the west of Sutlej Valley. Previously known from Simla Hills, Phagu, Theog, Matiana 8000-8700 ft., Nainital; Nepal; Manipur.

Protaetia orientalis (G. & P.)

1833. *Cetonia orientalis,* G. & P., *Monogr, Cet.* p. 193, pl. xxxiv, fig. 6
1910. *Protaetia orientalis,* Arrow in *Fauna Brit. India,* Coleop. Lamellicornia (Cetoniinae & Dynastinae), p. 143

1 male and 2 females from Dalhousie, 7500 ft. Punjab, Coll. M. S. Mani 22. vi. 1953.

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*Contribution No. 74 from the School of Entomology, published with the permission of the Professor of Zoology and Entomology.

The specimens before me differ from the published description in the absence of white marginal lines on each side of the pronotum; instead there is a series of opaque-white spots arranged in a line. The clypeus being not distinctly bilobed.

Previously known from Kashmir, China, Formosa, Japan.

Oxycetonia versicolor (F.)

1775. *Cetonia versicolor*, F., *Syst. Ent.*, p. 51
1910. *Oxycetonia versicolor*, Arrow, *Fauna. Brit. India*, Coleop. Lamellicornia (Cetoniinae, & Dynastinae), p. 164

1 male from Gurukul Kangri, Coll. C. S. Gupta, 21.ix. 1950. This species has previously been recorded from Silhet, Bhutan, Calcutta, Bannu, Mhow, Kanara, Malabar, Bengalore; Ceylon; Mauritius; Madagascar; Bourbon. This is the first record of the species from the Western Himalaya.

Oxycetonia albopunctata bivittata Burm.

1798. *Cetonia albopunctata*, F., *Ent. Syst. Suppl.* p. 129
1910. *Oxycetonia albopunctata bivittata*, Arrow in *Fauna Brit. India*, Coleop. Lamellicornia (Cetoniinae & Dynastinae), p. 167.

1 male from Gurukul Kangri, Coll. C. S. Gupta, 23.ix.1950. Although Arrow (loc. cit) has included this species as occurring within faunal limits of India, he does not mention the locality, where his specimens were collected.

Chiloloba acuta (Wied.)

1823. *Cetonia acuta*, Wied., *Zool. Mag.*, 2 (1) : 87.
1910. *Chiloloba acuta*, Arrow, *Fauna Brit. India*, Coleop., Lamellicornia (Cetoniinae & Dynastinae) p. 172.

1 male on gourd, Gurukul Kangri, Coll. C. S. Gupta, 20-ix-1950. Previously known from Sikkim, Dehra Dun, Landaur, Murree, Kangra Valley, Mhow, Belgaum, Bengalore, Malabar.

Clinteria spilota (Hope)

1831. *Cetonia spilota*, Hope, *Gray's Zool. Misc.*, p. 25
1910. *Clinteria spilota*, Arrow, *Fauna Brit. India*, Colep., Lamellicornia (Cetoniinae & Dynastinae), p. 184.

1 male and 2 females from Chakrata, Coll. Koshy Mathew, 21-ix-1953; Ramgarh, Coll. H. N. Baijal, 17-ix-1952.

The male from Chakrata with dark green partially metalic elytra; two females chocolate-red with elytra markings as in type. Previously recorded from Sikkim, Kurseong; Landaur, Mussoorie, Simla (7000 ft.), Rajpur (Bengal)

Macroma xanthorrhina (Hope)

1831. *Campsiura xanthorrhnia* Hope, *Gray's Zool Misc.*, p. 25.
1910. *Macroma xanthorrhina*, Arrow, *Fauna Brit. India*, *Coleop.*, Lamellicornia (Cetoniinae & Dynastinae), p. 219.

2 females from Chakrata, 8000 ft., Coll. Koshy Mathew, 20-ix-1953. Previously known only from Nepal, Sikkim, Darjeeling, Manipur, N. Khyen Hills (Burma). The species is being recorded here for the first time from the Western Himalaya.

Family RUTELIDAE

Popillia cupricollis Hope

1831. *Popillia cupricollis*, Hope, *Gray's Zool. Misc.*, p. 23.
1917. *Popillia cupricollis*, Arrow, *Fauna Brit. India*, Coleop., Lamellicornia, 2, p. 73.

2 females from Chakrata, Coll. R. S. Mathur, 20-ix-1953; and Ramgarh, Coll. H. N. Baijal, 17-ix-1952. Previously known from Kangra Valley, Kulu, Simla, Kasauli, Mussoorie, 7500 ft., Nainital, Kumaon, 6000 ft., Nepal, Sikkim, Kurseong, 5000 ft., Soom (Darjeeling distt.), Pedong (Assam).

Mimela passerinii Hope

1842. *Mimela passerinii*, Hope, *Proc. Linn. Soc.*, 1 : 128.
1917. *Mimela passerinii*, Arrow, *Fauna Brit. India*, Coleop.' Lamellicornia, 2, p. 105.

1 male and 2 females from Dalhousie, 7500 ft. Punjab, Coll. M. S. Mani, 17-vi-1953. Previously known from Sikkim, Darjeeling, Mungphu, Jallapahar, 7500 ft., Lachen Valley, 7000 ft., Kashmir, Campbellpore, Tibet, West China.

Mimela pectoralis Blanch.

1851. *Mimela pectoralis*, Blanch., *Cat. Coll. Ent. Mus. Paris.* (1850), p. 197.
1917. *Mimela pectoralis*, Arrow, *Fauna Brit. India*, Coleop., Lamellicornia, 2. p. 107.

1 male from Dalhousie, 7500 ft. Punjab, Coll. M. S. Mani, 21-vi-1953. Previously recorded from Lahore and Simla.

Mimela horsfieldi Hope

1836. *Mimela horsefieldi*, Hope, *Trans. ent. Soc. London*, 1. p. 114.
1917. *Mimela horsfieldi*, Arrow, *Fauna Brit. India*, Coleop., Lamellicornia, 2, p. 110.

1 male and one female coll. No. 567.2/55, 567. 3/55, from Katrain, 6000 ft., Coll. Santokh Singh, 24-vi-1955. Previously know from Jaintia Hills, Sibsagar (Assam), Ranikhet, Kusanie, 6000 ft., Kumaon, Kulu, Palampur, Simla, Nepal, Kurseong, Gowchar (Sikkim).

The specimens before me differ from the published description in the fiery-red bands on the elytra and other fierly spots on the body being inconspicuous.

Anomala auronitens (Hope)

1835. *Mimela auronitens*, Hope, *Trans. Ent. Soc. London*, 1, p. 114.
1917. *Anomala auronitens*, Arrow, *Fauna Brit. India*, Coleop. Lamellicornia, 2 : 242.

1 female from Ramgarh, Coll. H. N. Baijal, 17-ix-1952. Previously known from Kurseong, Mungphu (Sikkim), Manipur, Khasi Hills, Burma; Ruby mines. Generally common in the eastern Himalaya, the present record extends the range of distribution of this species to the western Himalaya.

Anomala stoliczkae Sharp

1873. *Anomala* (*Callistethus*) *stoliczkae*, Sharp, *J. Royal Asiatic Soc., Bombay,* 47 (2), p. 173.
1917. *Anomala stoliczkae*, Arrow, *Fauna Brit. India,* Coleop. Lamellicornia, 2 p. 243.

4 males and 3 females from Dalhousie, 7500 ft., Punjab, Coll. M. S. Mani, 14-vi-1953. Previously known from Murree, Jaunsar, Sikkim, Darjeeling, Tibet, West China.

Family CHRYSOMELIDAE

Dactylispa brevispinosa (Chap.)

1877. *Hispa brevispinosa*, Chapuis, *Ann. Soc. Ent. Belg.*, 22, p. 56.
1919. *Dactylispa brevispinosa*, Maulik, *Fauna Brit. India,* Coleop., Chrysomelidae (Hispinae & Cassidinae), p. 183.

Coll. No. 102.1/55, Manali, 6500 ft., Coll. V. K. Gupta, 23-v-1955; 576.21/55, Manali, 6500 ft., Coll. Santokh Singh, 25-v-1955. Previously known from Khasi Hill, 1000-3000 ft., Kangra Valley, 4500 ft. This is the first record of the species from the Kulu Valley.

Chrysomela populi L.

1758. *Chrysomela populi*, L., *Syst. Nat. ed.* 10, p. 370.
1926. *Chrysomela populi*, Maulik, *Fauna Brit. India,* Coleop. Chrysomelidae (Chrysomelinae & Halticinae), p. 68.

8 examples, Coll. Nos. 576.7/55-576.14/55 from Manali, 6500 ft., Coll. Santokh Singh, 25-vi-1955; 7 examples, Coll. Nos. 501.1/55-501.7/55, from Chhatru, 11,500 ft., Chandra Valley, Coll. Santokh Singh, 15-vi-1955; 3 specimens, Coll. No. 1 (1), Manali, 6000 ft. Kulu Valley, Coll. M. S. Mani & Santokh Singh, 2 -v-1954. Specimens from Chhatru, 11,500 ft. are slightly smaller and of lighter colour than from other localities. Previously known from Kashmir, 5200 ft., Dungagali (Hazara Distt.), 8000 ft., Matiana, Phagu, 9000 ft., Darjeeling, Ranikhet, 7000-9000 ft., Sukhtal (Kumaon), 8000 ft. Shillong. Originally described from Europe and also known from N. Africa and W. Asia, China and Japan.

Macrima armata Baly.

1878. *Macrima armata*, Baly, Cist. Ent., 2, p. 377.
1936. *Macrima armata*, Maulik, *Fauna Brit. India,* Coleop., Chrysomelidae (*Gallerucinae*), p. 561.

3 males and 2 females, Coll. Nos., 555.11/55-553. 12/55, Manali, 6500ft., Coll. Santokh Singh, 23-vi-1955; Coll. No. 567. 10/55-567.12/55, from Katrain,

6000 ft., Coll. Santokh Singh, 24-vi-1955. Previously known from Kashmir, Jhelum Valley, Kulu, Debrepani, 6000 ft. (Darjelling).

Merista sexmaculata (Koll. & Redt.)

1844. *Galleruca sexmaculata,* Koll. & Redtb., *in Hugel. Kaschmir und das Riech der Sick.,* 4. p. 555, fig. 5.
1936. *Merista sexmaculata,* in Mau lik, *Fauna Brit. India,* Coleop. Chrysomelidae (Gallerucinae), p. 145.

1 example from Chakrata, 8000 ft., Coll. R. Mathur, 18-ix 1953. Previously known from Kashmir, Muktesar, 75000 ft., Mussoorie, Almora, Nainital, Sunderdhunga valley, 8000-12000 ft., Kurseong, Gangtok, Gopaldhara, Orissa.

Merista quadrifasciata (Hope)

1831. *Galleruca quadrifasciata,* Hope, *Gray's Zool. Misc.,* p. 28.
1936. *Merista quadrifasciata,* in Maulik, *Fauna Brit. India,* Coleop. Chrysomelidae, (Gallerucinae), p. 149.

2 examples, Coll. Nos. 553. 4/55 from Manali, 6500 ft., Coll. Santokh Singh, 2 -vi 1955; 567.6/55 from Katrain, 6000 ft., cll. Santokh Singh, 24-vi 1956.

Previously recorded from Kashmir, Ladak, Kumaon, Bhimtal, Almora, Nainital, Simla, Nepal, Pharping, Gowchar, Soondrijal, Ranikhet, Muktesar, Mussoorie, Dehra Dun, Muree, 7500 ft., Kangra Valley, Abbotabad, Jeolikot Rungbong Valley, Gopaldhara, Mungphu.

Gallerucida bicolor (Hope)

1831. *Galleruca bicolor,* Hope, *Gray, Aool. Misc.,* p. 29.
1936. *Callerucida bicolor,* in Maulik, *Fauna Brit. India,* Coleop. Chrysomelidae (Gallerucinae), p. 554.

1 example, Coll. No. 567.7/55 from Katrain, 6000 ft. Coll. Santokh Singh, 24-vi-1955.

Previously known from Kangra Valley, Simla, Mussoorie, Dehra Dun, Garhwal, Lansdowne, Nepal, Sitong & Pashok (Darjeeling), Kalicut, Palghat, Mormugao (West Coast), Khasi Hills, Lower Burma.

STUDIES IN THE ARTIFICIAL GERMINATION OF POLLEN GRAINS :

1. GERMINATION OF POLLEN GRAINS OF SESBANIA ACULEATA PERS. AND CROTALARIA JUNCEA LINN.

By VED PAL SINGH, *Department of Botany, B. R. College, Agra.*

The process of improvement of Crop plants involves in general a systematic hybridization; the prerequisite for the success of which, however, is perfect compatibility between the two parents. Blakeslee[2] and Maheshwari[3] have enumerated various difficulties that possibly have to be encountered for successful hybridization. One of the usually experienced difficulties is the nonreceptivity of the stigma to the foreign pollen grains. This has been overcome variously, one being the application of suitable culture medium to the stigma to germinate the pollen grains. Recently Swaminathan[4] has used this method in overcoming the incompatibility in Solanum species.

The present author, while trying a cross between *Sesbania aculeata* Pers. and *Crotalaria juncea* Linn., found that only a small percentage of the pollen Grains of the former germinated on the stigma of the latter. The artificial germination of the pollen grains thus became necessary in view of the above difficulty.

MATERIAL ADD METHOD

The pollen grains of Crotalaria juncea and Sesbania aculeata were collected from the freshly dehisced anthers, and were put for germination in sugar agar medium prepared after Wulff and Maheshwari [5].

Slides with germinated pollen grains were fixed in formalinaceto-alcohol for three to five hours and stained in a combination of Heidenhain's iron-alum-haematoxylin and fast green. They were then dehydrated and mounted in balsam.

OBSERVATIONS

Sesbania aculeata : The germination of pollen grains of *Sesbania* started an hour after they were put in the culture medium of suitable concentrations. The table I gives the germination percentage and pollen tube length in microns in various concentrations of sugar agar. In 10% medium germination was fairly satisfactory but maximum germination was observed in 12% medium. The tube length attained in 5% and 7% sugar agar medium was much less and showed an increase with the rise in the concentration of sucrose upto 12%, where it was found to be 905μ (fig. 1). In 10% and 12% culture solution the generative nucleus was seen to divide in certain cases, while in others it had completed the division to form two male cells lying in the middle of the pollen tube or near its tip (fig. 2).

Table I

S. No.	percentage of sugar in culture media	Percentage of Pollen grain germination	Average length in microns
1	5%	5%	353
2	7%	17%	416
3	10%	49%	550
4	12%	75%	905

Crotalaria juncea: *Cortalaria* has got two types of anthers, round and long which outwardly show no difference in their pollen grains (Anant Rao and Gautam[1],). The pollen grains from these two types of anthers were put separately in culture media to find if there was any difference in their germination percentage and pollen tube size. Germination of *Crotalaria* pollen grains in 5% and 7% sugar agar media was negligible, while it was appreciable in 10% (Fig. 3) and it reached to a maximum in 14% medium. It was, however, interesting to find that the length of the tube was lesser in 14% medium than that in 10% where it attained the maximum length of 853 microns (Table II., Fig. 3). The division of the generative cell to form the two male cells was observed in all the grades of the culture medium when the tubes had attained a length of about 250μ (Fig. 4 and 5).

Table II

S. No.	Anther Type	Percentage of sugar in culture media	Percentage of pollen grain germination	Average length in microns
1.	Long	10%	71%	853
	Round	10%	73%	598
2.	Long	12%	72%	592
	Round	12%	79%	293
3.	Long	14%	65%	305
	Round	14%	84%	258
4.	Long	16%	52%	651
	Round	16%	64%	303
5.	Long	18%	42%	360
	Round	18%	51%	200

As stated above pollen grains from long and round anthers showed no difference in the external morphology. They, however, differed in their germination behaviour. The perusal of Table II, clearly shows that in culture media with 10-18% of sugar the pollen grains from round anthers showed comparatively a higher germination percentage over those from long anthers. But the pollen from long anthers showed comparatively longer pollen tubes in all cases. The pollen grains from the round anthers showed irregular width of the tube. The pollen tubes got swollen at their tips during germination and acquired the form of a bulb with the male cells lying in the bulbous tip (Fig. 5). This was particularly most marked in 14% and 16% sugar agar media.

The other peculiarity shown by the pollen grains from the round anthers is the sinuous coiling of the pollen tube. This behaviour is also shown by pollen from long anthers but in a very low percentage. The aforesaid sinuous coiling of the pollen tube from round anther has been observed in 18% of sugar agar medium (Fig. 6). The coiling started as soon as the tube emerged out of the pollen grain. In certain cases the coiling stopped midway while in others it reached up to the tip, where the coils were broadened and the tip became swollen. The male cells were also noticeable in the tubes which had coiled.

CONCLUSION

Pollen grains of *Sesbania* responded best in 12% sugar agar medium with respect to germination percentage and pollen tube length. The highest germination recorded is 70% with tube length measuring 905μ. The results obtained with *Crotalaria* pollen grains, however, differ from those of *Sesbannia* in having the highest germination percentage in 14% sugar agar medium (Germination 84%) but the largest tube length was attained in 10% (853μ).

The artificial culture of *Sesbania* pollen grains has revealed that 12% sugar agar gives the best results and if this solution is applied on the stigma of *Crotalaria*, it may prove helpful in getting a cross successful.

ACKNOWLEDGMENTS

My sincere thanks are due to Prof. Bahadur Singh and Dr. R. S. L. Paliwal for suggesting the problem and for guidance. I am also grateful to Dr. R. K. Singh, Principal, B. R. College, Agra, for facilities.

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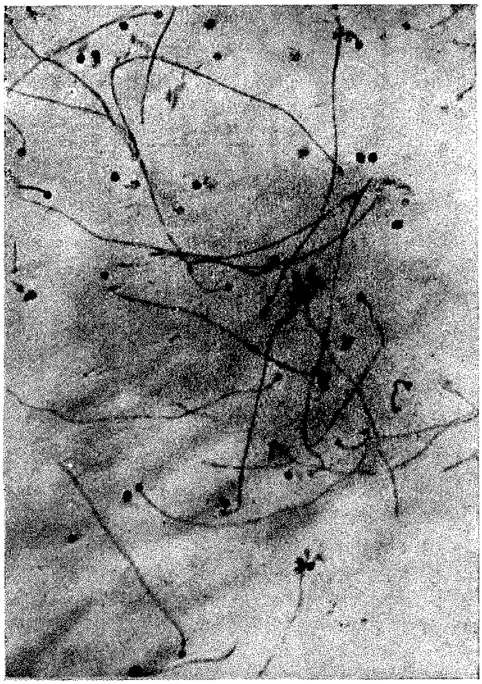

Figs. 1, Showing artificial germination of pollen grains of *Sesbania aculeata.* A low power view of germinated pollen grains. x90.

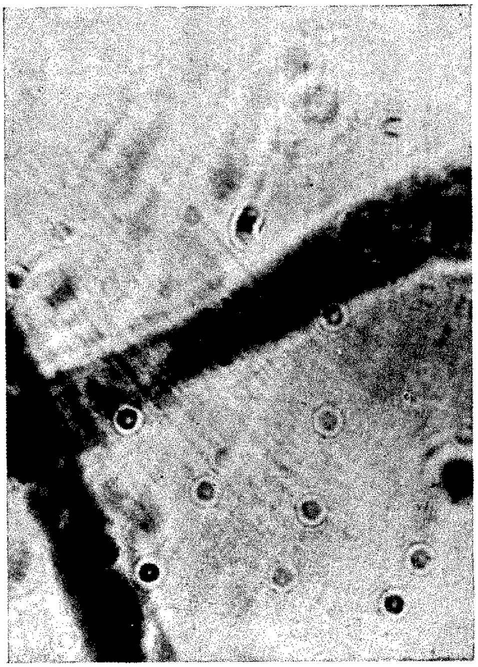

Fig. 2, Showing artificial germination of pollen grains of *Sesbania aculeata.* Part of the pollen tube showing two male cells. x1300.

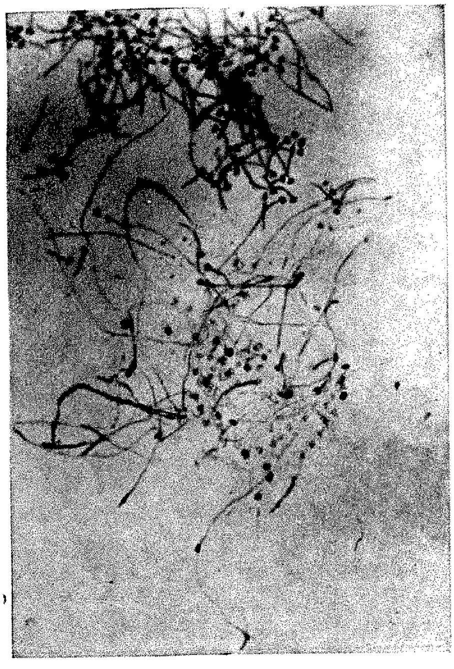

Fig. 3. Showing artificial germination of pollen grains of *Crotalaria juncea* A low power iew of germi- nated pollen grains. x60.

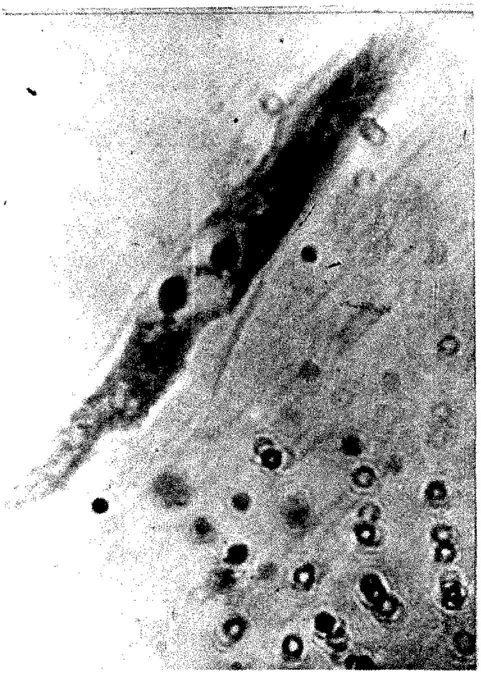

Fig. 4, Showing artificial germination of pollen grains of *Cratalaria juncea* A part of the pollen tube showing male cells x1700.

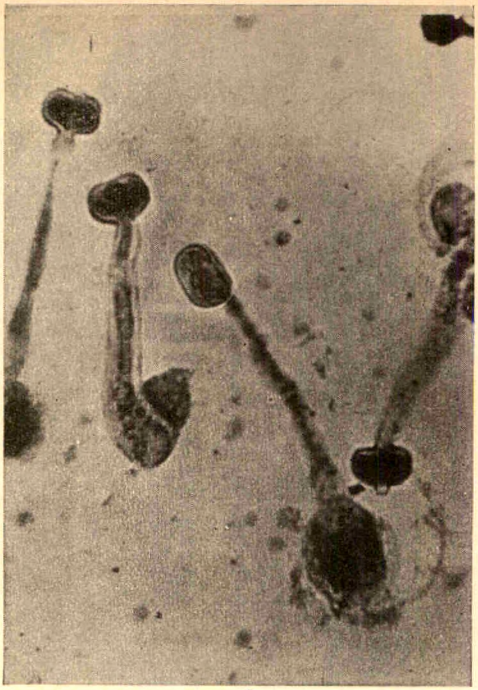

Fig. 5, Showing artificial germination of pollen grains of *Crotalaria juncea*. Pollen tube with swollen and bulbous tip harbouring two male cells. x450.

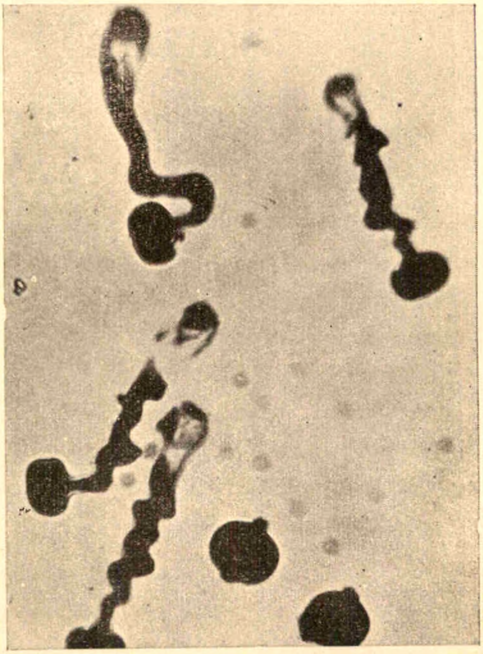

Fig. 6, Showing artificial germination of pollen grains of *Crotalaria juncea*. Pollen tube with sinuous coiling x375.

EFFECT OF GLUCOSE, NITRATE AND NITRITE INJECTIONS ON PROTEIN SYNTHESIS IN *ANONA SQUAMOSA* LINN. LEAVES*

By S. N. MATHUR, *Department of Botany, Meerut College, Meerut.*

Although a number of exhaustive reviews (9, 11, 12) have been published, and new methods of approach (1, 16), using radio-active isotopes, and analysis (15) are now known, our knowledge of Protein synthesis is still fragmentary. The reduction of nitrate to nitrite, hyponitrous acid, hydroxy lamine and ammonia has been suggested (4) in protein synthesis when inorganic nitrate is supplied. The present work was therefore, undertaken to investigate the effect of nutrients like Glucose, Nitrate, Nitrite and light on Protein Nitrogen, when injected into *Anona squamosa* leaves (8).

MATERIAL AND METHODS

A. squamosa was selected, for Bhattacharya (2) had found a fair amount of nitrate and nitrite in its leaves which are centres of great metabolic activity and are easy to inject. Healthy leaves were selected for analysis from Oct. to Jan. each time from the same plant.

Solutions of Glucose, Potassium nitrate and nitrite with and without Glucose were injected into fresh leaves following the technique of Roach (14). One set of injected leaves was kept open in the diffused light in the laboratory while another set was placed in a dark chamber for 24 hrs. Six series of experiments with control, Glucose, Nitrate and Nitrite (alone and in combination) injected leaves were performed and all determinations were made in excised leaves after 24 hrs. In the Glucose injected leaves total Nitrogen was determined by the Macro Kjeldahl method following Loomis and Shull (7), while in the leaves injected with Nitrate and Nitrite different fractions of Ammonia, Nitrate and Nitrite and Protein Nitrogen were determined by the modified Salicylic thiosulphate method (7) All results are based on fresh weights.

EXPERIMENTAL RESULTS

Solutions of 0.5-4.0% Glucose were injected into the excised *A. squamosa* leaves. The results are given in Table II. On comparison with control values in Table I, it is evident that the percentage of Total Protein-N was higher in glucose injected leaves varying from 4.0-5.2 in light and 4.0-4.8. in dark, while the corresponding values in control leaves were 3.8 and 3.7 respectively.

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* Paper read in the seminar on "Modern Developments in Plant Physiology" at the University of Delhi, Aug. 26, 1957.

Of the Nitrate, 0.5-3.0% solutions, alone and in combination with Glucose tried, besides Protein-N various fractions of Ammonia, Nitrate and Nitrite-N were also determined, as shown in Tables III & IV. In this case NH_3, NO_3 and NO_2 and Protein-N varied from 0.05-0.08, 0.10-0.14 and 4.0-4.7 respectively in light and 0.01-0.07, 0.07-0.10 and 3.9-4.1 in dark. These values when compared with the control ones in Table I are much higher. Nitrate in combination with glucose gave still higher values as they varied from 0.04-0.08, 0.11-0.15 and 4.0-5.3 in light and 0.01-0.06, 0.08-0.12 and 3.9-4.5 in dark.

However, Nitrite alone and in combination with glucose gave very low values specially of Protein-N. The various concentrations injected varied from 0.5-2.0. The fractions of NH_3, NO_3 and NO_2 and Protein-N in Nitrite injected leaves varied from 0.04-0.12, 0.17-0.24 and 1.7-3.8 in light and 0.04-0.12, 0.16-0.18 and 1.4-3.8 in dark. Nitrite in combination with glucose gave values, of 0.02-0.04, 0.08-0.16 and 1.0-2.8 in light and 0.02-0.04, 0.09-0.14 and 1.9-2.6 in dark. Though NH_3, NO_3 and NO_2-N fractions were higher, the Protein-N compared to control value, was considerably low.

DISCUSSION

It is clear from the data given in Table II that when a higher concentration of Glucose solution was injected, a higher percentage of Protein-N resulted. This percentage was more in light than in dark. Mothes (10) also found that when there was an opportunity for Carbohydrate synthesis in sunlight or the leaves had an available supply of glucose in dark, protein synthesis rather than hydrolysis predominated. In these glucose-injected leaves when they are placed in light, it may be assumed that besides protein synthesis, carbon assimilation is also taking place and is consequently supplying more protein-building units (1). On the other hand, in the leaves kept in total darkness, not only is carbon assimilation not going on and not providing C-skeleton, but also the protein break-down may have been rather quick. And this resulted in a lesser Protein-N (16).

The nitrate, in general, increased Ammonia, Nitrate and Nitrite and Protein-N. The Ammonia and Nitrate and Nitrite values, in partiular, were much increased. As the control leaves contained no trace of Ammonia (Table I), its presence in the injected leaves can wholly be attributed to injected nitrate. As regards the nitrate and nitrite content in the injected leaves, it is clear from Table III that besides the meagre amount originally present, there was a positive increase in its content, which can be explained only on the basis of its partial utilization during the metabolic process. What effect the nitrate injections have on the Protein-N, is also evident from the same Table. The control leaves had only a protein content of 3.8 in light and 3.7 in dark while the nitrate injected leaves show a variation of 4.0-4.7 and 3.9-4.1 in light and dark respectively. This increase in its value can best be explained as due to the stimulus given by the nitrate injections.

Further when nitrate was injected in combination with glucose, NH_3 and NO_3 and NO_2-N showed not much variation than when nitrate alone was injected but however, higher values of Protein-N were obtained as is evident inTable IV. Thus it may be concluded that if both carbon and nitrogen are available, more of Proteins are formed.

As nitrites are considered to form one of the intermediate products in the reduction of nitrate to form the complex protein, it was considered that nitrite nutrition might yield greater amounts of protein if it is supplied along with glucose, but these experiments proved otherwise. The Ammonia and Nitrate and Nitrite contents, however, increased enormously, as is clear from Tables V and VI, the Protein-N showed negative values. It is interesting to learn that the values were even much less than those in the control ones. According to Burkhart and Biekart (3), a high concentration of salts in the nutrient substrate, including even a high content of nitrogen, leads to carbohydrate accumulation and deficiency of elaborated nitrogen in the plant. It may, therefore, be concluded that the concentrations used were high enough as to retard protein synthesis. Further it may also be concluded that more proteins are formed in light than in dark (5, 13).

SUMMARY

1. Different concentrations of Glucose, Potassium nitrate and nitrite with and without Glucose were injected into *Anona squamosa* leaves of which one set was kept open in diffused light in the laboratory for 24 hrs. and another set in dark for the same period.

2. Only total-N was determined in Glucose injected leaves while in Nitrate, Nitrite with and without Glucose injected ones, besides Protein-N, NH_3, NO_3 and NO_2 -N were also determined. The same N-fractions were also determined after 24 hrs. in control leaves for comparison.

3. A high percentage of Protein-N was obtained in Glucose and Nitrate (alone and in combination) injected leaves, whereas this value was low in leaves injected with Nitrite with and without Glucose.

4. Finally the effect of Glucose and Nitrate in light has been found accelerating protein synthesis, while Nitrite retardlng it.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Professor V. Puri for his keen interest and encouragement, to Dr. I. M. Rao for suggestions in presentation of the text and to Professor R. Misra B.H.U. for going through the manuscript.

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NOTE:— Paper marked with asterisk was not available to the author in original.

Table I

Different Fractions of N in Control Leaves after 24 hrs.

In Light			In Dark		
% of NH_3-N	% of NO_3 & NO_2-N	% of Protein-N	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein-N
0.0	0.08	3.8	0.0	0.07	3.7

Table II

Effect of Glucose on Total Protein-N

% of Glucose Injected	% of Total Protein-N	
	In light	In Dark
0.5	4.0	4.0
1.0	4.0	4.2
2.0	4.2	4.1
3.0	4.5	4.3
4.0	5.2	4.8

Table III

Effect of Nitrate on NH_3, NO_3 and NO_2 and Protein-N in light & dark.

	In light			In Dark		
% of NO_3 Injected	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein N	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein N
0.5	0.05	0.10	4.0	0.01	0.07	3.9
1.0	0.06	0.11	4.1	0.05	0.08	4.0
2.0	0.07	0.12	4.5	0.07	0.08	4.0
3.0	0.08	0.14	4.7	0.07	0.10	4.1

Table IV

Effect of NO_3 and Glucose on NH_3, NO3 and NO_2 and Protein-N in light & dark.

	In Light			In Dark		
% of NO_3 & Glucose Injected	% of NH_3-N	% of NO_3 & NO_2-N	%of Protein-N	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein-N
0.5	0.04	0.11	4.0	0.01	0.08	3.9
1.0	0.05	0.12	4.5	0.03	0.10	4.0
2.0	0.07	0.13	4.9	0.05	0.10	4.2
3.0	0.08	0.15	5.3	0.06	0.12	4.5

Table V

Effect of Nitrite on NH_3, NO_3 and NO_2 and Protein-N in light and dark.

	In light			In Dark		
% of NO_2 Injected	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein-N	% of NH_3-N	% of NO_3 & NO_2-N	% of Protein-N.
0.5	0.04	0.17	1.7	0.04	0.16	1.4
1.0	0.08	0.19	2.0	0.05	0.19	1.7
1.5	0.10	0.22	3.3	0.06	0.17	3.0
2.0	0.12	0.24	3.8	0.12	0.18	3.8

Table VI

Effect of NO_2 and Glucose on NH_3, NO_3 & NO_2 and Protein-N in light & Dark.

	In Light			In Dark		
% of NO_2 and Glucose Injected	% of NH_3-N	% of NO_3 & NH_2-N	% of Protein-N	% of NH_3-N	% of NO_3 & NO_3-N	% of Protein-N
0.5	0.02	0.08	1.0	0.02	0.09	1.9
1.0	0.02	0.13	1.7	0.02	0.10	2.4
1.5	0.03	0.15	2.1	0.03	0.14	2.5
2.0	0.04	0.16	2.8	0.04	0.14	2.6

ENDOSPERM AND ITS CHALAZAL HAUSTORIUM IN CUCURBITACEAE

By Dalbir Singh*, *Bareilly College, Bareilly, India.*

Introduction

Recent morphological literature shows that the family Cucurbitaceae has attracted many workers. Singh (19 & 20) has described the seed structure in several members of the family. Puri (14) has studied the nature of placentae and placentation in Cucurbitaceae. Endosperm of the family has also received attention and many new features including the presence of a chalazal haustorium are reported (Chopra, 2, 3, 4 & 5; Johari and Roy Chowdhary, 8; Scott, 17 & 18; Singh, 21 & 22; and Weiling and Schagen, 23). Scott (17 & 18) has described the behaviour of the endosperm nuclei in *Echinocystis macrocarpa*. Singh (22) has recorded the formation of non-nucleated cytoplasmic nodules in some members of Cucurbitaceae. For a more comprehensive review of the chalazal endosperm haustorium in Cucurbitaceae refer to the paper of Chopra (5).

The present investigation was started in 1952 at the suggestion of Prof. Bahadur Singh, and the present paper is confined mainly to the presence and development of the chalazal endosperm haustorium in the following plants. Other important features viz., the presence of cytoplasmic nodules, observed in a number of these plants, and the behaviour of the endosperm nuclei are taken up elsewhere: *Benincasa hispida* Cogn; *Bryonopsis laciniosa* Naud; *Citrullus colocynthis* Schard., *C. fistulosus* Stocks; *Cucumis melo* L. var. *pubescens* Willd., *C.melo* var. *utilissimus* Field and Gard., *C. sativus* L; *Cucurbita pepo* L; *Coccinia indica* W. & A. (syn. *Cephalendra indica* Naud.); *Ctenolepis garcini* Naud. (syn. *Blastania garcini* Cogn.), *C. cerasiformis* Naud; *Cyclanthera explodens* Naud; *Echinocystis wrightii* Cogn; *Gymnopetalum cochinchinense* Kurz.; *Lagenaria vulgaris* Ser.; *Luffa acutangula* Roxb., *L. aegyptiaca* Mill; *Melothria lieosperma* Cogn., *M. maderaspatana* Cogn.; *Momordica balsamina* Linn., *M. cochinchinensis* Sprang; *Sechium edule* S. W.; *Thladiantha calcarata* Clarke; *Trichosanthes cucumerina* Linn., *T. dioica* Roxb.; and *Warea tonglensis* Clarke.

Material and Methods

The material of *Benincasa hispida*, *Citrullus fistulosus*, *Cucumis melo* var. *utilissimus*, *C. sativus*, *Cucurbita pepo*, *Lagenaria vulgaris*, *Luffa acutangula* and *L. aegyptiaca* was collected from the cultivated plants in the Botanical Gardens, B.R.

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*The work was completed during 1952-'55 when the author was at B.R. College, Agra. This paper is also prepared while working in the same department during the summer vacations.

College, Agra; while *Citrullus colocynthis*, *Coccinia indica*, *Ctenolepis cerasiformis*, *C. garcini*, *Melothria madraspatana*, *Momordica balsamina* and *M. cochinchinensis* were collected from the wild plants growing round about Agra. *Bryonopsis laciniosa*, *Trichosanthes cucumerina* and *T. dioica* materials were collected from Katiar (Bihar) and that of *Thladiantha calcarata*, *Sechium edule* and *Warea tonglensis* from Darjeeling. *Gymnopetalum cochinchinense* was collected from Teesta (about 40 miles from Darjeeling). The fixed material of *Cyclanthera explodens* and *Echinocystis wrightii* was kindly sent to me by Dr. E.J.H. Corner. *Melothria lieosperma* was collected for me by Mr. S. S. Ramam from Andhra.

Dissections were made under a dissecting microscope with a sharp blade and fine needles. The blade is used for making a slit parallel to the broad surface of the ovule from the chalazal to the micropylar end. The endosperm is excised with the help of needles. It is then stained with Belling's acetocarmine and mounted in Glycerine jelly.

The staining of microtome, as well as free hand sections, is done with Iron alum haemotoxylin, safranin and fast green or erythrosine and crystal violet.

ABBREVIATIONS USED

The following abbreviations are used in the text figures: ch, chalazal endosperm haustorium; e, embryo; en, endosperm proper and pt, pollen tube.

OBSERVATIONS

The endosperm of the family Cucurbitaceae is of free nuclear type (Figs. 1, 2, 6, 7, 15, 48, 55, & 62). After fertilisation the primary endosperm nucleus lies near the egg apparatus (Fig. 34); it may undergo division either in the same position (Figs. 32, 33, 35) or may travel to the centre of the embryo sac where it later divides (Figs. 46, 47). The resulting nuclei divide and form a large number of nuclei arranged in a peripheral lining. The centre of the embryo sac is occupied by a vacuole which is visible only in sections. The embryo sac before fertilisation is small in *Cyclanthera explodens* and many more plants while in *Thladiantha* and *Warea** it is quite long. (Figs. 32, 34). As the endosperm formation starts the embryo sac elongates considerably in *Cucumis*, *Cucurbita*, *Melothria*, *Sechium*, *Thladiantha*, *Trichosanthes* and *Warea;* and less so in *Ctenolepis*, *Benincasa*, *Citrullus*, *Cyclanthera*, *Gymnopetalum*, *Luffa*, *Momordica* and *Echinocystis*. In *Cucumis*,

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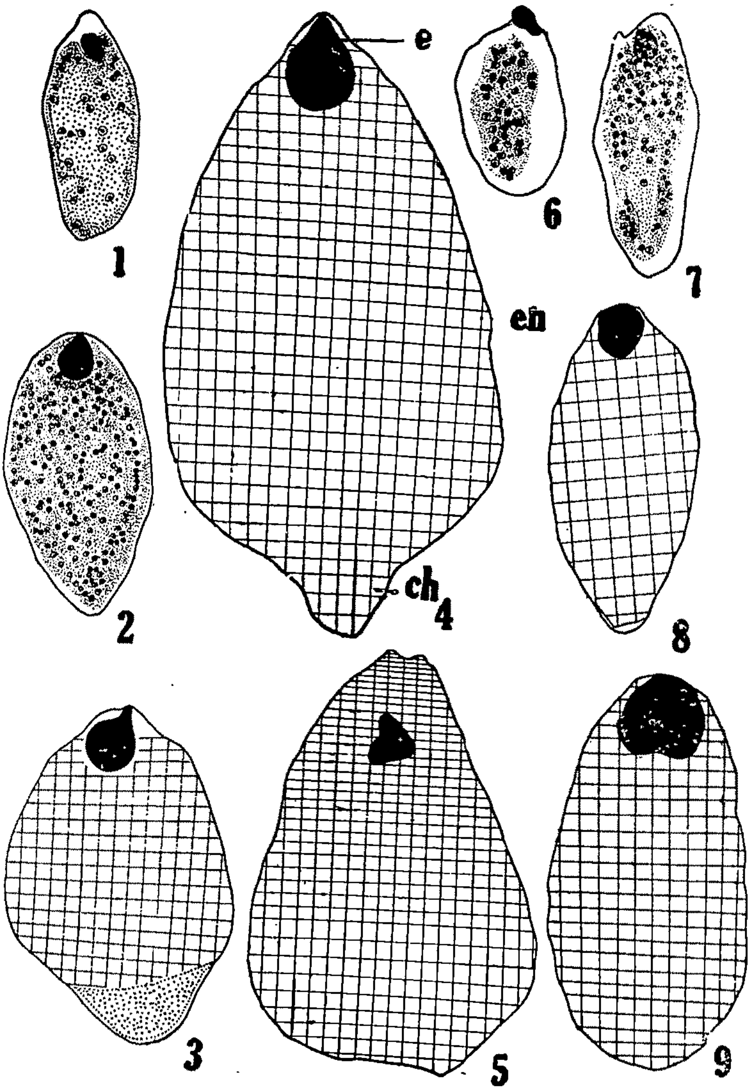
*Only young fruits were available.

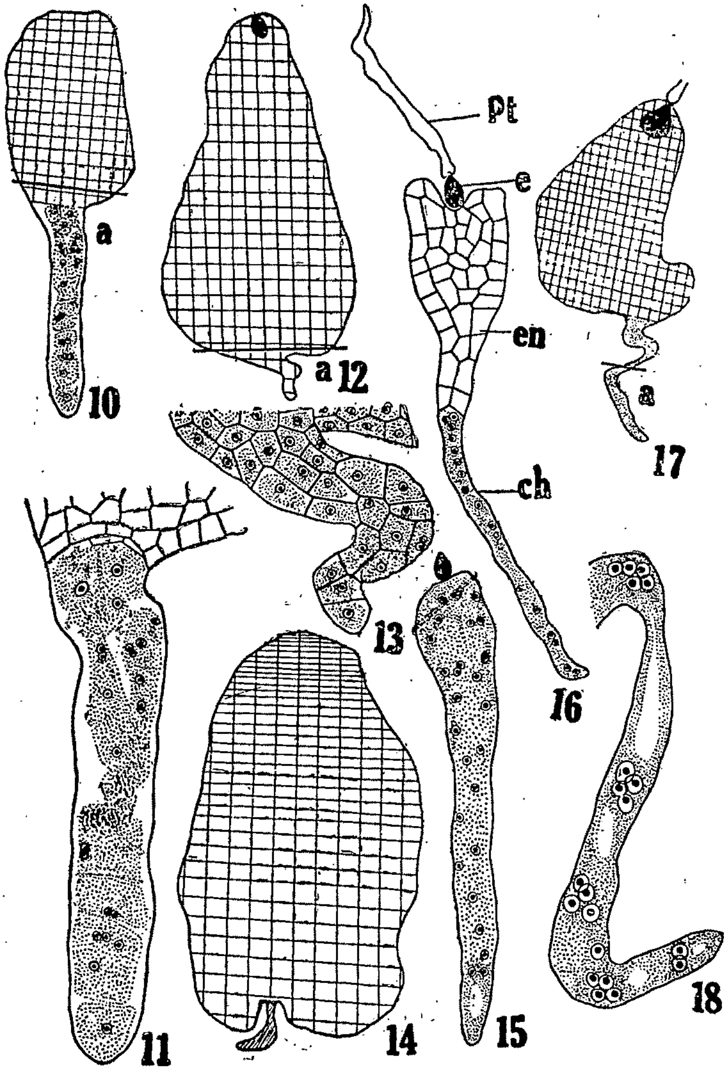
Cucurbita, *Melothria* and *Sechium* the growth of the embryo sac is very rapid.



Figs. 1—9.

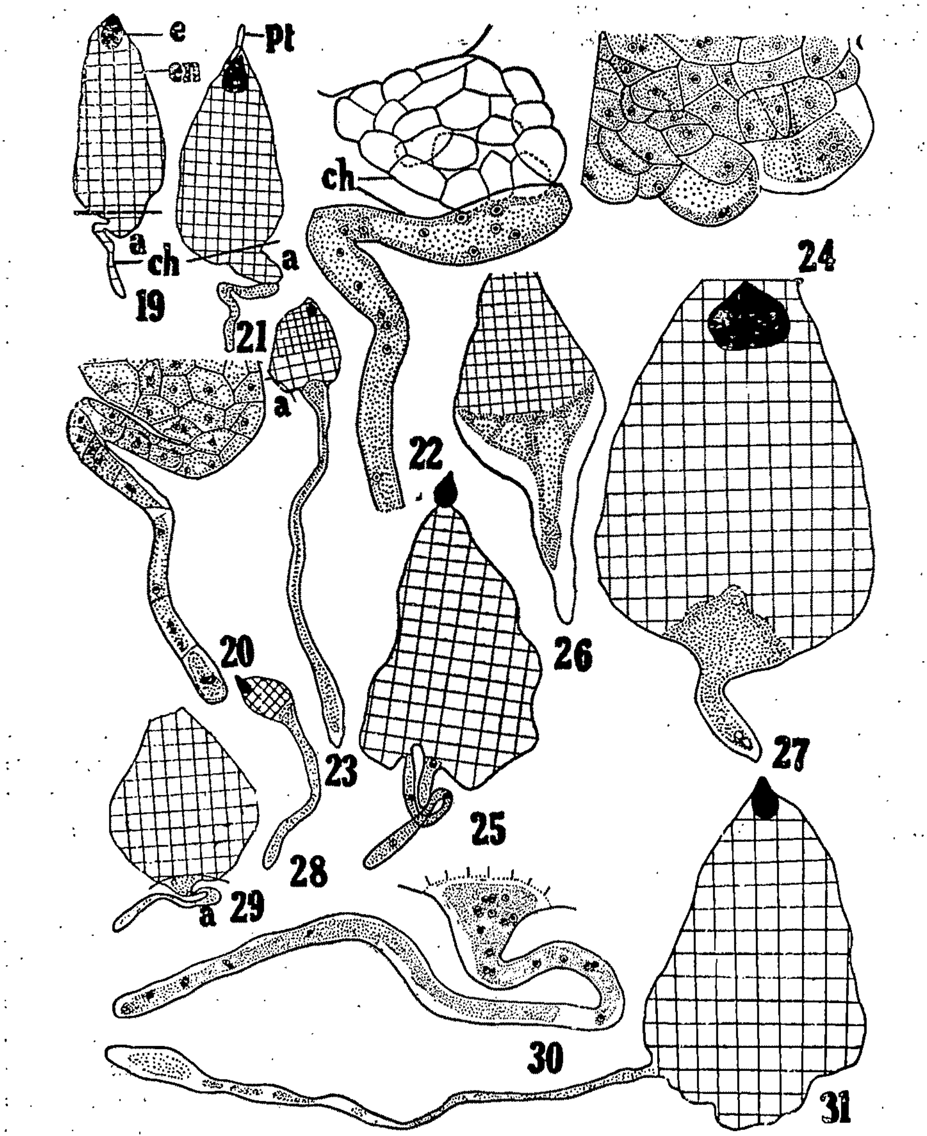
Figs. 1—5. *Ctenolepis cerasiformis*. Fig. 1. Free nuclear endosperm. x153. Fig. 2. Same, advanced stage. x113. Fig. 3. Endosperm, note the free nuclear part in the chalazal region. x113. Fig. 4. Endosperm showing cellular chalazal pouch. x113. Fig. 5. Endosperm, note the mixing of the cellular pouch with the endosperm proper. x25. Figs. 6-9. *C. garcini*. Figs. 6, 7. Free nuclear endosperm. x 113. Fig. 8. Cellular endosperm, note the narrow and pointed chalazal end. x113. Fig. 9. Endosperm, old stage. x72. (All figures from whole mounts; Figs. 3, 4, 5, 8, 9, diagrammatic).

As the endosperm grows further the embryo sac becomes broad at the base with a narrow caecum formed as its chalzal end (Fig. 15). The endosperm is thus clearly differentiated into a vesicular part and the chalazal haustorium (Figs. 10, 16, 23, 28, 31, 40, 44, 51, 57). The haustorium takes up a straight



Figs. 10—18.

Figs. 10—14. *Benincasa hispida*. Fig. 10. Endosperm with chalazal haustorium showing multinucleate compartments. x53. Fig. 11. Part 'a' from fig. 10. x153. Fig. 12. Endosperm with cellular haustorium. x29. Fig. 13. Part 'a' from fig. 12. x153. Fig. 14. Old endosperm, note the deformed chalazal haustorium. x 29. Figs. 15-18. *Citrullus colocynthis*. Fig. 15. Free nuclear endosperm. x 153. Fig. 16. Endosperm with free nuclear chalazal haustorium. x153. Fig. 17. Same, an advanced stage.x 29. Fig. 18. Part 'a' from fig. 17, note the aggregation of nuclei and their separation by vacuoles. x563. (Fig. 15 from section, rest all from whole amounts; Figs. 10, 12, 14, 17 diagrammatic).



Figs. 19-31.

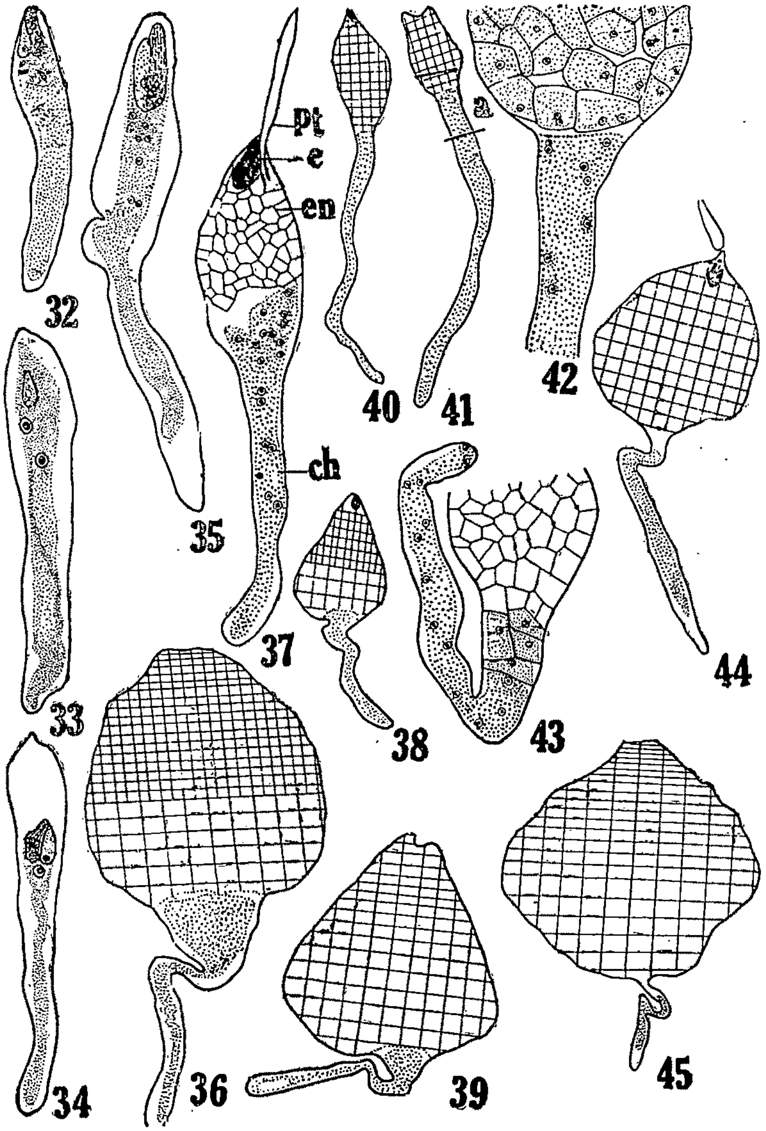
Figs. 19-22. *Ccccinia indica.* Fig. 19. Endosperm with cellular chalazal haustorium. x29. Fig. 20. Part 'a' from fig. 19. x153. Fig. 21. Endosperm showing a marked cellular portion between the endosperm proper and free nuclear haustorium. x29. Fig. 22. Part 'a' from fig. 21. x153. Figs. 23, 24. *Cucumis sativus.* Fig. 23. Endosperm showing chalazal haustorium, note the bulbous base of the haustorium. x12.5. Fig. 24. Cells from the chalazal part of main endosperm showing bulging. x113. Fig. 25. *Lagenaria vulgaris.* Endosperm, note the presence of two chalazal haustoria. x29. Figs. 26., 27. *Momodica cochinchinensis.* Fig. 26. Endosperm showing wall formation. x 29. Fig. 27. Same, old stage. x29. Figs. 28-30. *Momordica balsamina.* Fig. 28. Endosperm with chalazal haustorium. x12.5. Fig. 29. Same, note the bulbous base of the haustorium. x12.5. 8. Fig. 30. Part 'a' from fig. 29. x53. Fig. 31. *Cucurbita pepo.* Endosperm with *chalazal haustorium.* x17. (All figures from whole mounts, Figs. 19, 21, 23, 25, 26, 27, 28, 29, 31 diagrammatic).

course in the nucellus and brings about the destruction of the nucellar cells. In *Coccinia indica, Citrullus* and *Thladiantha,* the cells of the hypostase are distinguished from the rest of the nucellar cells. These cells near the embryo sac are smaller and their walls are cutinised. They persist at the tip of the haustorium forming a cup like structure in which the haustorial tip lies. Similar pockets of nucellar cells are reported in *Citrullus fistulosus* (Chopra, 5), *Apodanthera undulata, Citrullus citrullus* and *Cucumis myriocarpus* (Kirkwood, 10).

Wall formation starts in the endosperm only after the embryo has reached several celled stage. It is interesting to find that the vesicular part of the endosperm becomes cellular while the chalazal haustorium may either remain free nuclear throughout its life or it may ultimately become cellular much after the vesicular part has acquired the cellular structure. The wall formation starts near the embryo and extends from the periphery to the centre of the embryo sac, until whole of the vesicular part has become cellular (Figs. 26, 27, 37, 51, 56, 59), some of which remain multinucleate. The time required to complete the wall formation differs considerably in different plants. Usually it is short but in *Momordica cochinchinensis* it takes a longer time and the wall formation in this species is not quite complete even when the embryo has become heart shaped (Fig. 27). The cellular endosperm continues to increase in size both by cell division and cell enlargement. In some plants the endosperm cells in the chalazal region are bigger than those of the micropylar so that the two zones can be easily distinguished specially in *Cucumis sativus* and *Thladiantha calcarata* (Figs. 23, 36). Similar Condition is shown by *Gymnopetalum cochinchinense* at a younger stage (Fig. 38) and *Melothria lieosperma* rarely at older stages (Fig. 52). In many others the change is gradual and not so evident and in still others there is no difference in cell size.

The general form of the haustorium differs considerably in different species and rarely in the same species also. *Ctenolepis cerasiformis* shows probably the smallest haustorium in the form of a tiny pouch (Fig. 4); while genera like *Cucumis, Cucurbita, Melothria* and *Sechium* show a long tubular haustorium (Figs. 23, 31, 49, 51, 57). In *Cucumis sativus, Echinocystis wrightii, Gymnopetalum cochinchinense, Momordica balsamina* and *Thladiantha calcarata* the chalazal caecum rise from the main endosperm in the form of a bulbous free nuclear base which elongates into a narrower caecum (Figs. 23, 30, 36, 39, 60, 61).

The chalazal caecum occupies the central position at the base of the endosperm and it retains this position in majority of cases. In some plants, however, because of asymmetrical development of the main endosperm, it is pushed to one side and thus bcomes more or less lateral (Fig. 19, 21, 31, 52). Ocasionally such condition is also observed in *Citrullus colocynthis* (Fig. 17).



Figs. 32—45.

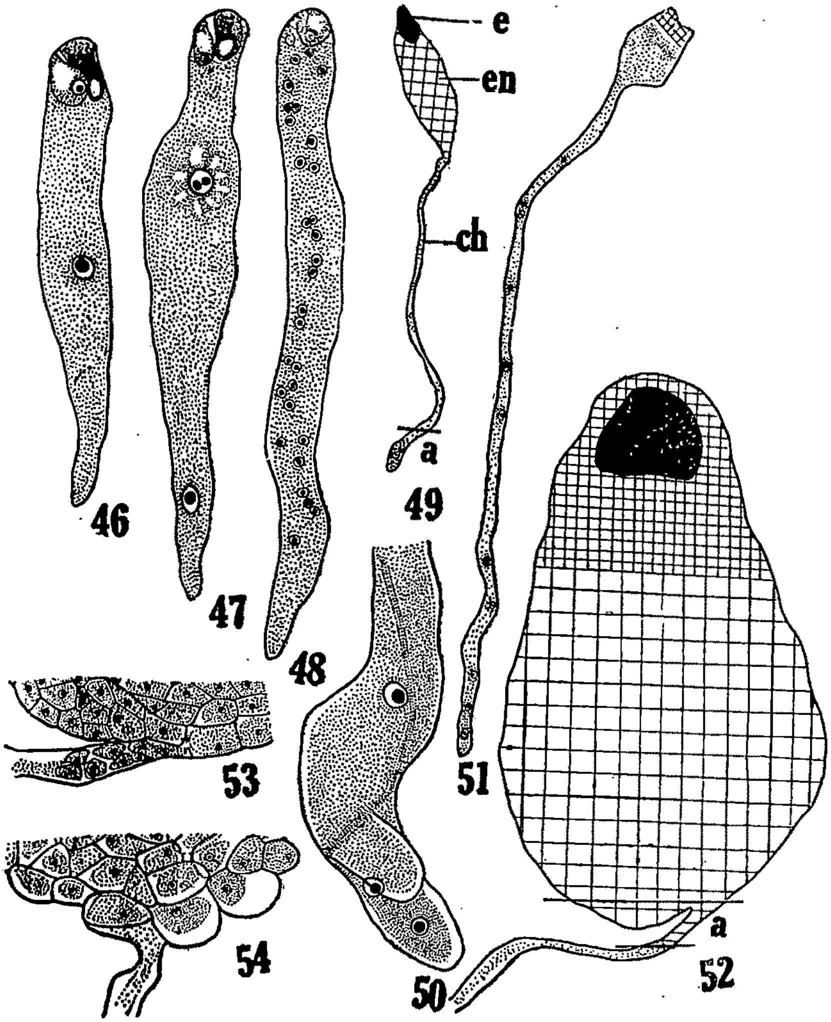
Figs. 32, 33. *Warea tonglensis*. Early stages of endosperm development. x53. Figs. 34-36. *Thladiantha calcarata*. Fig. 34. Embryo sac after fertilisation. x53. Fig. 35. Free nuclear endosperm. x53. Fig. 36. Endosperm with chalazal haustorium, note the bulbous base. x25. Figs. 37-39. *Gymnopetalum cochinchinense*. Fig. 37. Endosperm with chalazal haustorium. x113. Fig. 38. same, note the difference in cell size in micropylar and chalazal part. x25. Fig. 39. Same, old stage, note the bulbous base of the haustorium x25. Figs. 40-43. *Bryonopsis laciniosa*. Figs. 40, 41. Endosperm with chalazal haustorium. x25. Fig. 42. Part 'a' from fig. 41. x113. Fig. 43. Part of the endosperm showing cells in the proximal part of the endosperm haustorium. x113. Fig. 44. *Luffa acutangula*. Endosperm showing chalazal haustorium. x29. Fig. 45. *Trichosanthes dioica*. Endosperm with chalazal haustorium. x17. All figures from whole mounts; Figs. 36, 38, 39, 40, 41, 44, 45 diagrammatic).

The chalazal haustorium, to start with, is coenocytic in all the plants and becomes more prominent after the wall formation of the main endosperm and in the early stages it shows dense cytoplasm with several free nuclei. In *Echinocystis*, however, the number of nuclei in the haustorium is quite small (Fig. 61). In *Ctenolepis cerasiformis* and *Citrullus fistulosus* the haustorium becomes cellular (Fig. 4). In *Cyclanthera explodens* also it is mostly cellular (Figs. 63, 64) while *Coccinia indica* it is usually cellular (Figs. 19, 20) but rarely a part or whole of the caecum may remain free nuclear (Figs. 21, 22). In *Benincasa hispida* the haustorium becomes cellular formed of either multinucleate or uninucleate compartments (Figs. 10, 11, 12, 13). In plants other than described above, the haustorium always remains free nuclear. *Citrullus colocynthis* is, however, interesting in showing the chalazal haustorium with nuclei aggregated in groups only separated by vacuoles (Fig. 18).

The nature of the chalazal haustorium in the members of the Cucurbitaceae as shown in the present investigation is given in the tabular form for ready reference:

Name	Remarks
Benincase hispida	Mostly cellular
Bryonopsis laciniosa	Mostly free nuclear
Citrullus colocynthis	Free nuclear
C. fistulosus	Cellular
Coccinia indica	Mostly cellular
Ctenolepis cerasiformis	Cellular
C. garcini	Huastorium absent
Cucumis melo var. *pubescens*	Free nuclear
C. melo var. *utilissimus*	Free nuclear
C. sativus	Free nuclear
Cucurbita pepo	Free nuclear
Cyclanthera explodens	Mostly cellular
Echinocystis wrightii	Free nuclear
Gymnopetalum cochinchinense	Free nuclear
Lagenaria vulgaris	Free nuclear
Luffa acutangula	Free nuclear
L. aegyptiaca	Free nuclear
Melothria lieosperma	Mostly free nuclear
M. maderaspatana	Free nuclear
Momordica balsamina	Mostly free nuclear
M. cochinchinensis	Free nuclear
Sechium edule	Free nuclear
Thladiantha calcarata	Free nuclear
Trichosanthes cucumerina	Free nuclear
T. dioica	Free nuclear
Warea tonglensis	

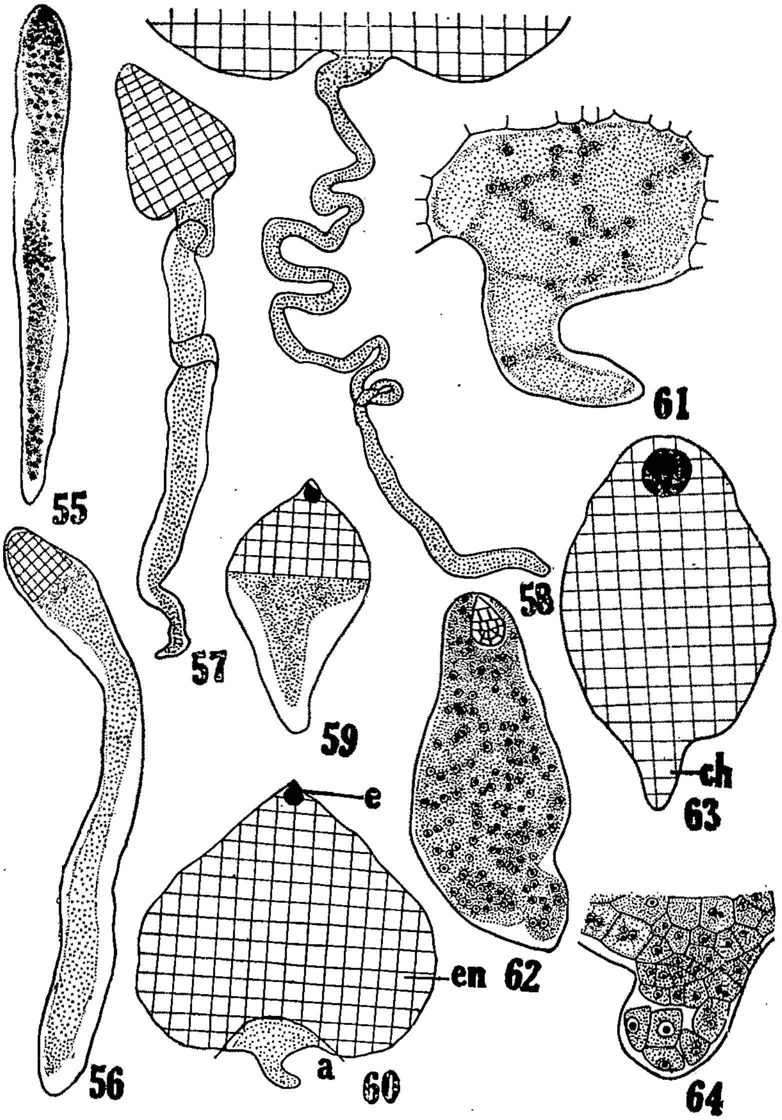
Certain abnormalities are also met with in the structure of the haustorium. Normally the haustorium remains free nuclear in *Bryonopsis laciniosa*, *Melothria lieosperma* and *Momordica balsamina* (Figs. 30, 41, 42, 54), but sometimes its proximal part becomes cellular while the distal remains free nuclear (Figs. 3, 53). In *Coccinia indica* in one case a marked cellular part was observed between the main endosperm and the coenocytic haustorium (Figs. 21, 22). In *Cyclanthera explodens*, where a short cellular haustorium is found, in a single case a prolongation of the cytoplasm was observed near the chalazal end, suggesting that in this species the haustorium may be occasionally a tubular, elongated and coenocytic structure. *Lagenaria* endosperm sometimes shows the presence



Figs. 46—54

Figs. 46—50. *Melothria maderaspatana.* Fig. 46. L. S. embryo sac with primary endosperm nucleus. x153‘ Fig. 47. L. s. embryo sac showing two endosperm nuclei. x 153. Fig. 48. L. s. free nuclear endosperm. x153. Fig. 49. Endosperm with chalazal haustorium. x29. Fig. 50. Part 'a' from fig. 49, note the branched tip oj the haustorium, x563. Figs. 51-54. *M. lieosperma.* Fig. 51. Endosperm showing vesicular part and the tubular chalazal haustorium. x53. Fig. 52. Endosperm with coenocytic haustorium showing cells in the proximal part. x53. Fig. 53. Part 'a' from fig. 52. x113. Fig. 54. Part of the endosperm, note the coenocytic haustorium. and bulging of cells. x113. (Figs. 49-54 from whole mounts,) Figs. 49, 51, 52 diagrammatic).

of two chalazal haustoria (Fig. 25), the small tubular haustorium is a prolongation of one of the bulged out peripheral cells. In *Melothria maderaspatana* the tip of the chalazal haustorium was observed to have branched in one case (Fig. 50).



Figs. 55-64.

Figs. 55—58. *Sechium edule*. Fig. 55. Free nuclear endosperm. x23. Fig. 56. Endosperm showing wall formation. x23. Fig. 57. Endosperm with free nuclear haustorium. x12.5 Fig. 58. Part of the endosperm showing coiled haustorium. x12.5. Figs. 59-61. *Echinocystis wrightii* Fig. 59. Endosperm showing wall formation. x29. Fig. 60. Endosperm with chalazal haustorium, note the bulbous base, x12.5. Fig. 61. Part 'a' from fig. 60. x53. Figs. 62-64. *Cyclanthera explodens*. Fig. 62. Free nuclear endosperm. x113. Fig. 63. Cellular endosperm, with chalazal pouch. x53. Fig. 64. Part of the endosperm, showing chalazal haustorial pouch. x230. (All figures from whole mounts, Figs. 56, 57, 58, 59, 60, 63 diagrammatic).

The haustorium remains healthy up to the development of the heart shaped embryo. In advanced stages the contents of the coenocytic haustorium disappear which shrinks but remains attached to the endosperm (Figs. 29, 36, 39, 45, 58). In *Benincasa* and *Coccinia*, where the chalazal haustorium is cellular but tubular and well differentiated from the endosperm proper, the cell contents disappear and the haustorium becomes deformed (Fig. 14). In *Citrullus fistulosus* and *Cyclanthera explodens*, where mostly the chalazal haustorium is cellular it remains quite healthy and disappears only with the main endosperm. *Ctenolepis*, however, shows the amalgamation of the tiny haustorium with main endosperm during its later stages of develoment (Fig. 5).

As the activity of the haustorium declines, the peripheral cells of the main endosperm in the chalazal region bulge out (Figs. 24, 54). The feature is more marked in *Benincasa hispida, Citrullus colocynthis, Coccinia indica, Cucumis sps., Cucurbita pepo, Echinocystis wrightii, Gymnopetalum cochinchinense, Lagenaria vulgaris, Luffa acutangula, L. aegyptiaca, Melothria lieosperma, Thladiantha calcarata* and *Trichosanthes* sps.; and less so in others. *Citrullus fistulosus, Ctenolepis sps.* and *Momordica cochinchinensis* do not show any such bulging. The cells show large vacuoles and granular cytoplasm suggesting their haustorial function and have been termed as "Secondary haustoria " (Chopra, 5). The degree, of bulging, however, considerably differs in different plants. Bulging of peripheral cells has also been reported in *Grevillia robusta* (Kausik, 9) where also a coencytic chalazal caecum is present. A point significant regarding these secondary haustoria or bulged cells is their better development in plants with coenocytic, tubular and mostly elongated haustoria. It may be remarked that the coenocytic, elongated and tubular haustorium appears to be more efficient for absorption, with more absorbing surface and bring about better translocation of the collected food material. Complete absence of the bulged cells or their poor development in those plants which normally possess a short and cellular haustorium is difficult to explain on the secondary haustorial theory. Occasionally when these plants develop tubular and coenocytic or with multinucleate compartments haustorium, bulging of the peripheral cells at the base of endosperm also becomes quite evident. Thus *Citrullus fistulosus* where the haustorium is short and cellular, bulging is not observed; but *C. colocynthis* with a tubular coenocytic haustorium, shows marked bulging. *Momordica cochinchinensis*, with coenocytic tubular haustorium, is an exception where bulging of the peripheral cells is absent, but in this plant he main endosperm is enormous in size. It is to be considered if the bulging of the peri pheral cells is purely haustorial or it is due to the collection of the absorbed food material by the chalazal endosperm haustorium.

In older stages the main endosperm increases greatly in size and is ultimately consumed by the growing embryo. In mature seeds only a few outer most layers, or mostly a few degenerating cells near the tips or between the cotyledons, may persist.

The endosperm development in the two species of *Ctenolepis* ie. *C. cerasiformis* and *C. garcini* is described in detail separately because of some differences in observation. Recently Chopra (3 & 5) has reported the absence of the haustorium in *Blastania garcini* (syn. *Ctenolepis garcini*). In *C. cerasiformis* the free nuclear endosperm is oval as shown in Fig. 1. As further development takes place the chalazal end becomes narrow and pointed (Fig. 2). During the wall formation a free nuclear chalazal region is demarcated (Fig. 3), which later becomes cellular (Fig. 4). At the globular embryo stage a cellular pouch is quite distinct in the chalazal region, but during further growth of the endosperm it is amalgamated with the main endosperm and, therefore, become inconspicuous (Fig. 5). In *C. garcini* the endosperm is observed to show a somewhat similar development (Figs. 6, 7, 8, 9).

Discussion

Chopra (3, 4, 5) has shown the causes why the chalazal endosperm haustorium has been missed or inadequately presented by the previous workers. The author from a study of both sections as well as dissections, also concludes that sections always do not present a complete picture of an organ and consequently fail to present complete details. This explains why most of the previous workers, who mainly studied through sections only, could not arrive at proper understanding of the structure. Only a few of them have figured a tube like prolongation of chalazal end of the endosperm. Brongniart (1) in *Pepo macrocarpus*, Mirbel (13) in *Cucumis leucantha*, Amici* in *Cucurbita pepo* and Garreau (7) in *Cucumis sativus* has drawn similar structure. Schnarf (15), while reviewing the endosperm of the Cucurbitaceae, has reported a chalazal tubular haustorium in Citrullus *citrullus*, *Apodanthera undulata*, *Sicyos angulata* (Kirkwood, 10) and *Cucurbita pepo* (Longo, 12; Kratzer, 11) and further in a later publication has written of the similar structure in first two plants (Schnarf, 16). Kirkwood (10), who has studied 15 species, mentions such a structure in *Apodanthera undulata*, *Citrullus citrullus* and *Fevillea cordifolia*. A careful study of his paper, however, reveals that in the above mentioned plants he has reported a chalazal tubular prolongation of the endosperm, while in many others he refers a thin cytoplasmic strand developing from the chalazal end of the endosperm, the morphology of those thin cytoplasmic strands is not fully understood. For *Cucumis myriocarpus* Kirkwood (10) writes "The endosperm elongates in the direction of the chalaza as soon as fertilisation has taken place............The lower part, however, is a very delicate film which terminates in a sort of cup like collections of cells like that shown in the case of *Apodanthera*." Similar delicate cytoplasmic strands have also been reported in *Benincasa hispida*, *Melothria pendula*, *Momordica charantia* and *Sicyos angulata*, while in the rest he does not mention any such structure. He has also referred to the pocket of nucellar cells in *Apodanthera*, *Citrullus* and also in *Cucumis myriocarpus*.

The present study of the two species of *Ctenolepis* reveals a definite cellular chalazal pouch in *C. cerasiformis*. In *C. garcini*, however, the endosperm at the globular embryo stage presents only a narrow chalazal portion and no clear haustorial pouch. It is thus in agreement with Chopra (3 & 5). During further growth in both the species the chalazal pouch or narrow end amalgamates with the main endosperm. The presence of the tiny haustorium in *Ctenolepis cerasiformis* may be due to the reduction or it may even represent the beginning of the origin of the haustorium in Cucurbitaceae. A similar cellular chalazal pouch is also mostly formed in *Cyclanthera explodens.*

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*Quoted in Facchini (6).

The endosperm is free nuclear and the wall formation takes place after many nuclei are formed. Chopra (2) has mentioned that "It may be simultaneous as in *Citrullus* and *Coccinia* or may progress from apex downwards as in *Momordica*." In another paper Chopra (3) has described the endosperm of *Blastania, Coccinia, Citrullus* and *Cucumis* does not make any reference to this point. Later on, however, he states that "It is simultaneous in *Lagenaria, Luffa,* and *Trichosanthes,* where as in *Momordica* it progresses from apex downwards," Chopra (4). In his recent paper Chopra (5), mentions about the wall formation in the endosperm that, "It progresses downwards and centripetally," and further "The mode of wall formation has been observed in *Citrullus fistulosus, Momordica charantia* and *Cucumis sativus*." No doubt he earlier commented on the mode of wall formation in *Coccinia* (Chopra, 2), *Lagenaria, Luffa* and *Trichosanthes* (Chopra, 4,), but he does not refer to them in a later publication (Chopra, 5). The present author has studied the wall formation in many plants of the family and finds that it is always progressive and initiates near the embryo to progress downwards centripetally. It is, however, observed that the time taken to complete the wall formation in the main endosperm differs considerably in different genera.

The endosperm possesses a chalazal haustorium in all the members studied except *C. garcini* (see preceeding table). The haustorium may be cellular as in *Benincasa, Citrullus, Coccinia, Ctenolepis* and *Cyclanthera;* and it remains coenocytic in the rest. Chopra (5) seems to have not quite correctly quoted Kirkwood (10) when he mentions that the chalazal haustorium becomes cellular in *Citrullus citrullus.* Schnarf (15) while summarising the endosperm of Cucurbitaceae has written, "Bei *Citrullus citrullus* ein langes, Schlauchformiges chalazales Haustorium, in welchem frei Endospermkerne liegen and niemals Zellbuilding eintritt; similar is his statement in his later publication (Schnarf, 16). In *Citrullus fistulosus* (Chopra, 5) and *C. colocynthis* (Johari and Roy Chowdhary, 8) the cellular haustorium is also reported. Under the present study it is observed that it becomes cellular in *C. fistulosus,* but in *C. colocynthis* it remains free nuclear, only aggregation of nuclei and their separation by vacuoles is observed. Rare abnormalities in the structure of the chalazal haustorium are also shown as described in the observations. It is noticed that the chalazal endosperm haustorium is cellular in cases where it is short, and even in these plants when it is elongated it forms either only multinucleate compartments, as in *Benincasa hispida,* or remains coenocytic in *Coccinia indica* and *Cyclanthera explodens.* This fact reveals that the size of the haustorium plays an important part in ascertaining its ultimate form, whether cellular or free nuclear.

It is interesting to find the difference in the final behaviour of the haustorium. In plants with coenocytic haustorium it loses its contents, shrinks and becomes inactive before the consumption of the main endosperm. In *Benincasa* and *Coccinia* where it is cellular, the cells of the haustorium are disorganised before the consumption of cells of the main endosperm. The cases of *Citrullus fistulosus*, *Ctenolepis cerasiformis* and *Cyclanthera explodens* are some what different. In *Citrullus* and *Cyclanthera* the chalazal haustorium remains quite healthy and is consumed by the growing embryo like the rest of the endosperm, while in *Ctenolepis* the haustorium gets completely amalgamated with the endosperm proper.

The plants investigated under the present study include members from the five tribes of the Cucurbitaceae ie. Fevilleae Melothrieae, Cucurbiteae, Sicyoideae and Cyclanthereae all of which show the presence of the chalazal haustorium.

SUMMARY

Endosperm development has been studied in 17 genera including 26 species, in all the plants except *C. garcini* the presence of the chalazal endosperm haustorium is recorded.

The endosperm development is of nuclear type. After fertilisation the embryo sac elongates and during further development the free nuclear endosperm is distinguished into a vesicular upper part termed as the "endosperm proper" and an elongated tubular chalazal process referred to as "chalazal haustorium" in majority of the cases. In *Ctenolepis* and *Cyclanthera* the chalazal process is represented only by a small pouch or mound.

The wall formation in the endosperm proper progresses downwards and centripetally. The chalazal haustorium is free nuclear with dense cytoplasm in earlier stages. Subsequently the haustorium may become cellular in *Benincasa, Citrullus, Coccinia, Ctenolepis* and *Cyclanthera;* and in rest remains free nuclear throughout its life. In *Cucumis sativus, Echinocystis wrightii, Gymnopetalum cochinchinense, Momordica balsamina* and *Thladiantha calcarata* the chalazal caecum arise from the endosperm proper in the form of a bulbous free nuclear base.

The haustorium finally disappears in majority of the plants much before the consumption of the endosperm, but in *Citrullus fistulosus, Ctenolepis* and *Cyclanthera* it is used along with the main endosperm. As the activity of the haustorium declines the peripheral cells show bulging. Finally the embryo consumes whole of the endosperm leaving only a few cells either between or near the tips of the cotyledons and also sometimes laterally.

The haustorium is recorded in the members of all the tribes of Cucurbitaceae ie. Fevilleae, Melothrieae, Cucurbiteae, Sicyoideae and Cyclanthereae.

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SOCIAL FACTORS IN THE AETIOLOGY OF ASCARIASIS IN CHILDREN IN BHOPAL

By Dr. P. S. Mathur, M.D., D.C.H., *Lecturer, Gandhi Medical College, Bhopal.*

The large intestinal nematode *Ascaris lumbricoides* owes its specific name to its resemblance to the common earth-worm; Greeks and Romans designated it as *Lumbricoides teres.* Since ancient times it has been recognised and described by Zoologists. Davine* in 1863 observed that its ingested ova are hatched in the human intestine. In 1916 Stewart* discovered the indirect cycle of its larvae through the lungs in mice and rats. Ransom and Foster* in 1917, and later Ransom and Cram* in 1921, showed that after the preliminary pulmonary cycle the larvae of *Ascaris suum* developed into adult worms in the intestine of the hog, and Koino* and Kóino in 1922 traced a similar migration in men.

As Ascariasis is very common in Bhopal, a detailed study of all the cases of Ascariasis dealt with in the Pediatrics Department of Hamidia Hospital was undertaken with a view to eliciting the socio-economic status of the parents and the living conditions of the affected children. These included infants and children up to the age of 12 years. The stools of all these cases were examined as a routine and the history of passage of the worm was taken.

During the period January-December 1956, 7500 cases attended the Pediatrics Department of Hamidia Hospital, Bhopal. Out of these 600 cases i.e., 8 per cent were found suffering from ascariasis as confirmed by the appearance of the worm in 467 cases and detection of the ova in 133 cases. All these children; however, had not come for symptoms connected with ascariasis. Only 540 children were brought for symptoms suggestive of ascariasis; the remaining 60 cases were suffering from indigestion, pain in abdomen, alternate constipation, diarrhoea and chronic cough; and the detection of ascaris infection was incidental.

Incidence in relation to social class

In every case studied, social status of the father was determined and classified according to monthly income, number of family members, living standard, and hygienic condition of surroundings. Those with a monthly income of Rs. 50/- or less and with crowded living space and dirty sanitary conditions were classified as the lowest socio-economic group IV; those with a monthly allowance of Rs. 50/- to Rs. 100/- and similar or slightly better living conditions as the poor socio-economic Group III; Rs. 100- to Rs. 300/- as the middle socio-economic group II; and those with an income above Rs. 300/-

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* Cited by David L. Belding, "Text-book of Clinical Parasitology".

per month and living under good hygienic surroundings as the socio-economic group. I.

Out of these 600 cases, it was not possible to assess the socio-economic status of 50 cases with certainty. The result of the investigation into the remaining 550 cases is tabulated below:—

TABLE I

Incidence of 550 cases of ascariasis according to socio-economic groups

Social class	*No. of cases*	*Percentage*
Upper Socio-Economic Group I	15	2.7
Middle Socio-Economic Group II	40	7.3
Poor Socio-Economic Group III	195	35.5
Lower Socio-Economic Group IV	300	54.5
	550	100

Thus 495 out of 550 cases (i.e. 90 per cent) of all children with ascariasis came from the socio-economic groups III and IV, where the family income was less than Rs. 100/- p.m. and the home environments were poor, unhygienic and otherwise unsatisfactory.

Incidence in relation to their residence

The hospital caters to the needs of the town of Bhopal, outer colonies of the town and rural population in the surrounding villages. Out of the total attendance of 600 cases of ascariasis in the department of Pediatrics during the year 1956, 390 (i.e., 65 per cent) belong to Bhopal town; 120 (i.e. 20 per cent) came from outer colonies of the city; and 90 (i.e. 15 per cent) came from rural areas. The 600 cases under investigation were analysed from the point of view of the locality of residence. It was found that 390 lived in the heart of the city, while the rest were from the outer colonies of the city and from rural areas.

TABLE II

Analysis of 600 cases according to residence

	No. of cases	*Percentage*
Residents of Bhopal Town	390	65
Residents of adjoining colonies	120	20
Residents of rural areas	90	15
Total	600	100

It thus appears that in this part of the country ascariasis is much more common in town-dwellers than in children living in the rural areas. The areas, in which it is common, are very thickly populated.

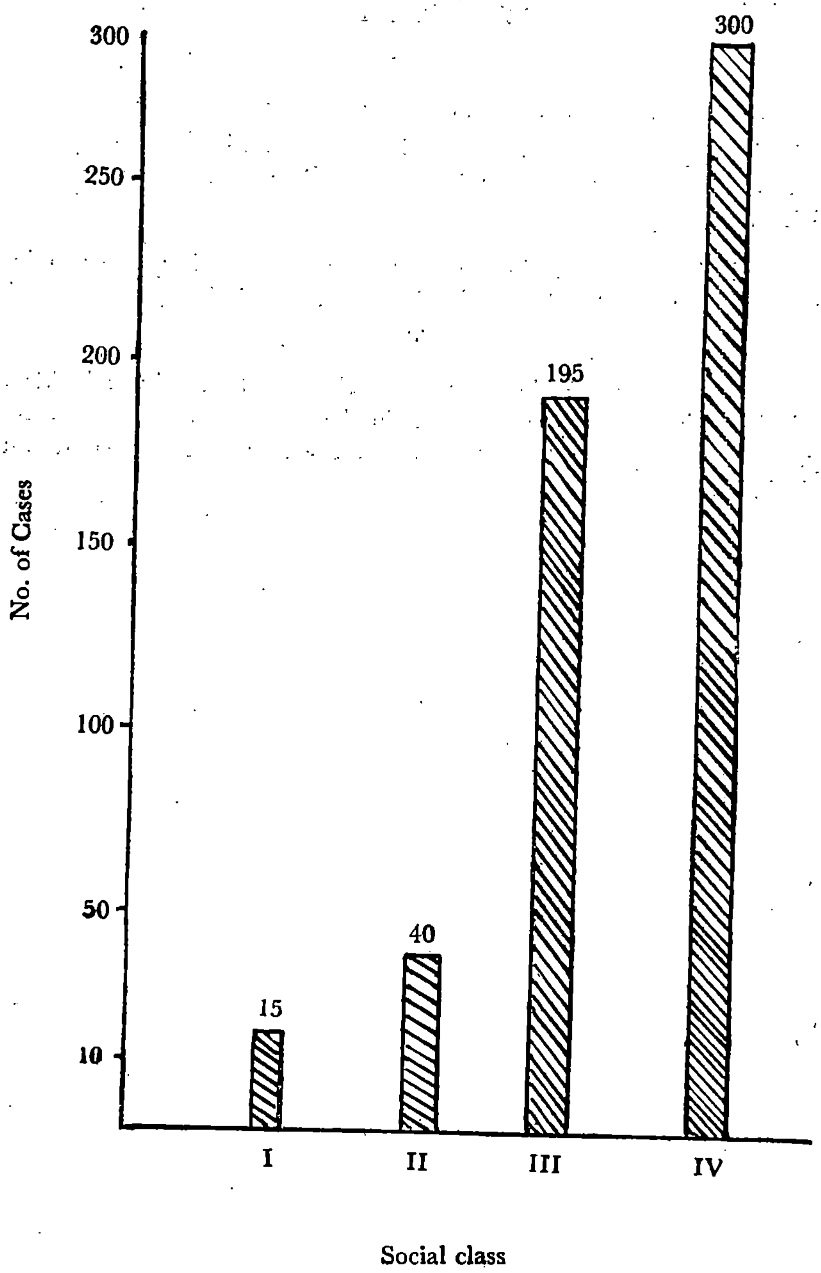
SUMMARY

It has been shown that out of the children with ascariasis who attended the Pediatrics Department of the Hamidia Hospital an unduly high proportion came from families belonging to the Socio-Economic groups III and IV, members of which are mostly unhygienic in their habits.

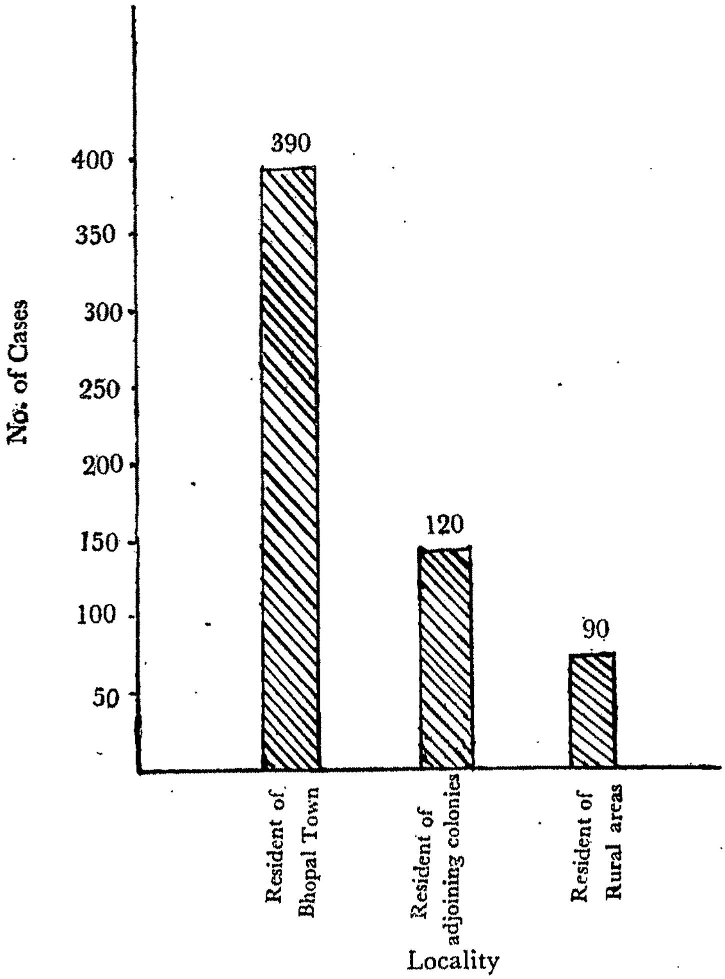
The incidence of ascariasis among the children living in the main city is high, indicating thereby that the incidence of ascariasis is closely associated with bad sanitation and overcrowding.

It seems reasonable, therefore, to conclude that the higher incidence of ascariasis found in the larger towns and in the lower social classes is related mainly, if not entirely, to the factors of overcrowding, bad sanitation and unhygienic habits.

Graph of Table I



Graph of Table II



EMBRYONIC DEVELOPMENT OF MYLABRIS PUSTULATA THUNB.

By Dr. S. R. Deobhakta, *Department of Zoology, Agra College, Agra.*

This paper summarises the results of my three and a half years' study of the general embryonic development of *Mylabris pustulata*, a beetle that serves a common class-room type.

In the course of this study, I have been able to trace the complete series of developmental stages, almost upto the hatching of the larva, without any major gaps.

I take this opportunity of recording my sincere thanks to Professor M.S. Mani, D.Sc., School of Entomology St. John's College, for suggesting the problem and for guidance. I am indebted to the Ministry of Education, Government of India, for the award of a Senior Research Scholarship which enabled me to carry out this work.

1. THE EGG

A brief account of the oviposition has already been published by me (16). Egg laying begins with the onset of rains in July and continues almost upto the end of September. A single female lays on an average (3—4) batches of eggs. As mentioned earlier (*loc. cit.*), each batch contains an average of 200-300 eggs but the number of eggs falls off in successive batches. The egg clusters are thrust in cavities at a depth of about half an inch in loose damp garden soil. The method of the formation of the egg chamber has also been described earlier.

Freshly-laid eggs are white but at the end of a day their colour changes to pale yellow. Just before hatching the eggs are brown. The eggs are all glued together by a sticky coating, secreted at the time of oviposition. This coating seems also to have the effect of retarding the dessication of the eggs. The size of the egg is about 1.38 mm. long and .48 mm. thick, but as development proceeds a slight increase in size may be observed. For further details of the structure of the egg reference may be made to my paper cited above.

With regard to the maturation and fertilization, already described, it may be noted that the miosis is completed within the ovary. The haploid nucleus measures about 60 microns and lies a little behind the micropyle. The two polar bodies gradually disintegrate and no trace of them is seen immediately after the oviposition.

2. CLEAVAGE

Cleavage may be observed in eggs fixed within fifteen minute of oviposition. The general course of the fragmentation of the zygote nucleus is more or less similar to the process described in most other Coleoptera. The nuclear fragments migrate rapidly to the posterior and equatorial region of the ovum, but reach the anterior end only at a very late stage. The nuclear fragments reach the posterior mass of peripheral protoplasm by about ninth hour of incubation but the anterior end is reached only after the twentieth hour of incubation. The cleavage may be said to be practically completed within twenty four hours after incubation. For further details regarding the course of cleavage reference may be made to my paper published in 1954 (17).

At the end of cleavage the nuclear fragments which have migrated to the periphery of the egg and have come to lie beneath the vitelline membrane, show indications of the blastoderm formation. Summarising the accont of the formation of blastoderm, given on page 447 of my paper referred to above, the first indication of lastoderm become apparent at the thirtieth hour of incubation. The peripheral protoplasm begins to condense round each nuclear bits. The outer boundaries of the blastoderm cells become soon apparent. Intercellular constrictions deepen six hours later. The definitive cells of the blastoderm are visible at the 48th hour of incubation. The blastoderm forms a continuous layer except at the posterior region of the egg where cell fomation is not still completed or the cells are not arranged in a definitive layer.

The nuclear fragments are spherical and a dense cytoplasmic envelope surrounds them. In about an hour of incubation the number of the nuclear fragments increases greatly and are confined to the anterior one-fourth of the egg. The condensation of cytoplasm around these nuclear fragments is cosniderable at this time. Further rapid divisions are taking place and the migration of the nuclear fragments is more rapid towards the posterior region and rather slowly towards the egg periphery and the anterior region.

At about the sixth hour of incubation the number of nuclear fragments has further increased and most of them reach nearly upto the middle of the egg. The cytoplasmic envelope round each fragment has become denser.

At the ninth hour the nuclear fragments reach the posterior end and penetrate the oösome. The nuclear bits entering oösome increase in size, the cytoplasm seems to condense round each bit. These nuclear bits are the so called "germ track determinants."

The entire egg is traversed by the migrating nuclear fragments which reach very near to the periplasm on the dorsal and ventral sides of the egg, but do not reach the periplasm at the anterior end and are deeper within the reticuloplasm.

After ten hour of incubation the nuclear fragments enter the periplasm in the middle of the egg. Only a few fragments have entered in the periplasm the majority of the fragments lie just beneath the periplasmic envelope of the egg. In the anterior end the nuclear fragments are still far away from the periplasm and this is the region where the nuclear fragments enter last of all. The so-called germ-track determinants' further increase in size and show a distinct backward Shift.

The nuclear fragments in the anterior end reach close to the periplasm at the twelfth hour of incubation. In the equatorial zone the number of nuclear fragments entering the periplasm is very large and some of them have come to lie just under the vitelline membrane. The so-called 'germ track determinants' have further shifted backwards and the majority of them come to lie in close contact with the vitelline membrane. A few of them even bulge out conspicuously.

At fifteenth hour the cleavage nuclei penetrate the periplasm in the anterior end. Their number in the equatorial zone has increased further, the majority of the nuclei are in contact with the vitelline membrane. The indications of a regular arrangement of the nuclear bits are already evident.

After twenty hours of incubation the nuclear fragments have penetrated in the periplasm at the anterior end of the egg. In the middle the nuclei have oriented in a regular layer. Those nuclei which do not enter the periplasm but remain behind within the reticuloplasm constitute the vitellophags.

At twenty-four hours the nuclei arrange themselves in a more or less regular layer, their size is relatively small and they undergo a few rapid divisions, so that just beneath the vitelline membrane there is closely packed multinucleate periplasm everywhere except near the posterior end of the egg.

3. Formation of the blastoderm

The zygote nucleus after undergoing rapid and repeated fragmentation which have moved to the periphery results in the formation of an enormous synicitical mass enclosing the yolk. At the thirtieth hour of incubation the first indication of the division of the peripheral cytoplasm becomes evident. The outer boundaries of the cell walls are first to become apparent. Six hours later the boundaries between the adjacent cells become distinct. At about forty-eighth hour the definitive cells of the blastoderm are complete. The blastodermal cells appear columnar in sagittal sections. Throughout the entire surface the blastoderm is fully organised except at the posterior end where the 'germ-track determinants' are located. The inner cell walls of the blastoderm are last to appear.

A detailed account of cleavage and the formation of the blastoderm has been published in the Agra University Journal of Research, Vol. III (Science), pp. 441-448, July 1954.

1. Germ Band

As briefly described earlier (*loc. cit*) the formation of t
becomes distinct in the postero-ventral region at the 60th hou
and steadily extends forward. The cells of the germ-band are la
but anteriorly pass gradually into the ordinary blastoderm cells
end of the germ-band is slightly curved over the posterior e
end it is separated from the blasotderm cells by the presenc

determinants." When first forming the germ band is relatively small and occupies only short length of the postero-ventral end of the egg. A pronounced increase in length nearly upto the middle of the egg may be clearly observed after about 8 hours. There is also a lateral expansion of the germ-band.

When the germ band has been fully formed, the "germ track determinants" can no more be distinguished as such and it has not been possible to study their fate. The posterior end of the germ band is still curved round the posterior egg pole and is now in continuation with the rest of the extra-embryonal area of the blastoderm. The yolk cells are scattered throughout the central yolk mass and their number has increased considerably. This increase is brought about by further repeated divisions of the yolk cells which were left behind during the peripheral migration of the cleavage nuclear fragments. No peripheral nuclei were seen to migrate back into the central yolk mass. Such a migration of the nuclear framents back into the central yolk mass has so far been observed among Coleoptera only in the case of *Brachyrhinus* by Butt (8). The direct division of the yolk cells has been recorded among Coleoptera by Tiegs and Murray (150) in the case of *Calendrc.* At a later stage the yolk cells appear to disintigrate in the yolk and no trace of them has been observed in the remains of yolk at the end of embryonic development.

2. FORMATION OF THE VENTRAL GROOVE

A preliminary account of the formation of the inner layer was published in 1954 (17). About 72 hours after oviposition the ventral groove makes its first appearance. The first indications are distinctly seen in the posterior region. A small inward depression of the germ-band shown in Fig. VI, C and D in the paper represents this stage.

The formation of the ventral groove is restricted to the mid-ventral line of the germ-band. The groove is deepest posterriorly, shallow in the middle of the germ-band. A little behind the anterior end it is very shallow and is in the form of relatively wide trough-like invagination. The portion of the germ-band thus invaginated represents the middle plate and the portions on either side of the groove constitute the lateral plates. The posterior deeper
f the ventral groove show marked cell proliferations from the middle,
her regions of the groove are inactive so far. In the posterior most
epest part the proliferations of the cells from the middle plate is most
us the median ventral groove appears first posteriorly and then
xtends forwards. In the sagittal sections of the germ-band
oove is seen as a deep invagination of the germ-band and the cell
intense. The germ-band has shifted its position and its posterior-
not curve round the posterior pole of the egg. This
lue to the sinking-in of the germ-band along the mid-ventral
ventral groove. In doing so the posterior end is pulled

The ventral groove deepens further posteriorly. The groove becomes pronounced and gradually extends to the middle region of the germ-band at 75 hours of incubation (Fig. 3, plate 1). About the same time a somewhat faint invagination of the anterior part of the germ-band with slight cell proliferation may be observed. Posteriorly the cells proliferating from the ventral groove spread and the resulting cells become arranged across the entire breadth of the germ-band. In the middle shallow part of the ventral groove the cells still continue to proliferate actively but all the cells are not yet arranged across the breadth of the germ-band.

After 78 hours of incubation the inner layer has spread out uniformally beneath the entire length of the germ-band (Fig. 6, Plate 2). The germ-band is pushed into the yolk at the posterior end. Its anterior end is also pushed into the yolk but not so deeply in comparison to the posterior end. In a longitudinal section slightly to one side of the median longitudinal line of the germ-band the posterior region appears somewhat sunk inwards. This is due to the formation of the embryonic envelopes (Fig. 8, Plate 2), the folds of which are more pronounced posteriorly than in the middle or front part of the germ-band.

3. FORMATION OF THE PRIMARY DORSAL ORGAN

The primary dorsal organ makes its appearance at 72 hours of incubation about the same time as the ventral groove is formed. This organ developes opposite the middle of the egg on the dorsal side. The blastoderm is modified in the form of a samll cluster of cells projecting conspicuously into the yolk. The outer ends of these cells stain rather more deeply than the somewhat obscure inner ends. The primary dorsal organ persists upto 78 hours of incubation. This organ disintigrates into the yolk before the embryonic envelopes are fully developed. At 81 hours of incubation when the amnion and serosa are well formed there is no trace of the primary dorsal organ.

EMBRYONIC ENVELOPES AND BLASTROKINESIS

There are two embryonal evelopes viz. serosa and amnion. The serosa fully covers the egg below the chorion and the amnion covers the ventral surface of the embryo. After the differentiation of the germ-band, the extra-embryonal blastoderm assumes a more or less pronounced squamous nature, distinct from the characteristic columnar cells of the germ-band. About the 78th hour of incubation, the rudiments of amnion and serosa are first observed (Fig. 6, 8, Plate 2; AMN, SER). The posterior part of the germ-band gradually sinks inwards, so that the extra-embryonal epithelium gets folded forwards on the ventral surface of the germ-band. In the meantime the cells of the serosa also elongate and beocome more or less spindle-shaped. Thus the sinking in of the germ-band as well as the elongation of the cells of the serosa contribute to the formation of the post-amniotic fold (Fig. 8, Plate 2; AMN. F) which grows over a small portion of the germ-band at its posterior border.

A similar fold appears anteriorly at a somewhat later stage but it is not so pronounced. The sinking in of the germ-band into the yolk is rather faster and deeper posteriorly (Fig. 8, Plate 2) than anteriorly (Fig. 6, Plate 2), so that the germ-band becomes flexed inwards behind (Fig. 6, 8, Plate 2). During this process of insinking, the germ-band remains connected everywhere to the extra-embryonal area. With the progressive sinking of the germ-band, two lateral amniotic folds also arise (Fig. 7, Plate 2).

The cephalic, the lateral and the posterior folds approach to meet and fuse together in the mid-ventral line, so that ventrally the embryo is covered by amnion inside and serosa outside. The growth of the serosa is relatively more rapid than that of the amnion. At about 81 hours of incubation we may observe the fusion of the amniotic folds (Fig. 10, 12, 13, 14, Plate 3; AMN, SER).

Further development of the amnion depends on the blastokinetic movements and changes in shape of the germ-band. In the course of blastokinesis the germ-band lengthens conspicuously and the amnion also keeps pace. The complete development of the amnion is brought about by further sinking into the yolk of the germ-band. It is now a membrane covering the embryo ventrally, attached to it at the margins, but well separated enclosing a spacious amniotic cavity in the middle (Fig. 10, Plate 3; AMN.C).

The cells of the amnion are large and somewhat rounded (Fig. 10, Plate 3; AMN) and the amnion is comparatively short. It is only when the germ-band has attained its maximum length after the blastokinesis that the amnion becomes fine and membranous. The cells of the serosa become more or less spindle-shaped (Fig. 10, 14, Plate 3; SER) and their nuclei are large with coarse and sparse cytoplasm.

After the complete differentiation of these two embryonic envelopes the serosa is separated from the embryo, while the amnion alone remains connected. The yolk does not penetrate between the amnion and the serosal folds. The amnion and serosa are in direct contact in the mid-ventral line (Fig. 14, Plate 3; AMN, SER). The same condition has been found in certain other Coleoptera by Johannsen and Butt (68).

As typical in most other Coleoptera, the embryonic development of which has so far been studied, the germ-band is superficial and short and is almost confined to the posterior region of the egg in *Mylabris pustulata*. The blastokinesis is also not very pronounced. There is over-growth of the anterior and posterior amniotic folds as described by Graber (30) in *Lina*. The movements of the germ-band are almost wholly restricted to its hinder end, which alone becomes relatively deeply curved dorsally and immersed in the yolk. We thus find the typical features of the invaginated type of germ-band. This stage is rapidly succeeded by a gradual shifting forward of the germ-band as a whole, with a slight sinking of the anterior end also, as mentioned already. This anteriorly directed movement seems to have the effect of gradually pulling the curved and sunk posterior end out and straightening up of the germ-band that now comes to occupy a superficial position. When this condition has been reached, the rupture of the embryonal envelopes mentioned above is not yet complete.

More or less the same condition has been described in other Coleoptera such as *Hydrophilus* by Kowalevski (73) and Heider (44, 45, 46); *Lina* by Graber (30); *Doryphora* by Wheeler (156). The blastokinesis of May beetles, *Phyllophaga fervida* and *P. hirticula* described by Luginbill (88) has a different course. The germ-band first lengthens and its anterior end moves half the distance around the periphery of the anterior pole. After passing down the ventral side the posterior end curves round the posterior pole and anteriorly on the dorsal side until it has covered one-third the distance between the poles. Then the anterior and posterior ends of the germ-band withdraw to position along the mid-ventral line in the polar regions. This extension and retraction of the germ-band is called blastokinesis by Luginbill. In case of *Brachyrhinus*, described by Butt (8), here also it is the posterior end of the germ-band which sinks into the yolk.

At about 78 hours of incubation the anterior and posterior ends of the germ-band are pushed into the yolk (Fig. 6, Plate 2). The posterior end is however sunk much deeper into the yolk than the anterior. With this sinking of the germ-band into the yolk blastokinesis begins. At about 81 hours the posterior as end well as the anterior end of the germ-band sink still deeper into the yolk (Fig. 10, Plate 3), so that the germ-band as a whole is conspicuously curved inwards. The posterior end is in particular curved inwards and forwards.

Soon after at 85th hour of incubation the anterior end of germ-band draws out of the yolk and comes to lie again at the surface of the egg (Fig. 16, Plate 4), while the posterior end is still immersed inside the yolk. It is however not so curved as at 81st hour of incubration. The germ-band in the meanwhile has shifted forward and has come to lie more or less at the equator of the egg. There is however no real elongation of the germ-band.

After 94 hours of incubation the posterior end of the germ-band is fully withdrawn from the yolk. The anterior end has already been withdrawn from the yolk and the entire germ-band comes to lie at the surface (Fig. 32, Plate 7). The amniotic cavity is now more or less uniform throughout. The position of the germ-band at this stage has shifted considerably and extends to nearly two-thirds the egg length (Fig. 32, Plate 7), indicating slight growth in length also. At this stage the blastokinetic movements are over.

SEGMENTATION

The germ-band of insects shows superficial segmentation at about the time the germ layers develop. The metamerism appears first in the transversely divided mesoderm and later in the transverse grooves formed in the ectoderm. Eastham (18, 19) has however stated that in the case of *Pieris* the ectodermal segmentation precedes the mesodermal. Soon after its formation the germ-band divides into a broader head region the protocephalon or the region of the procephalic lobe bearing the eyes, antennae, mouth and the labrum. The posterior region, which is narrower than the protocephalon and is known as the protocorm gives rise to the jaw-segments or the mouth parts of the head, thorax and the abdomen. The protocorm undergoes segmentation, beginning with the anterior end. Among Coleoptera segmentation begins in *Brachyrhinus* and *Stenobothrus* in the thorax and then proceeds both forward and backward. In the Chrysomelid beetle *Donacia* according to Hirschler (59) the germ-band first divides into a procephalic and three protocormic elements, wherein the inner layer has undergone segmentation into four parts roughly corresponding to the external primary segmentation. The same condition has been observed in the case of *Locusta* by Roonwal (126, 127). Other examples of the primary segmentation have been described for *Meloe* by Nusbaum (104, 105).

The segmentation of the germ-band may appear as early as the very beginning of gastrulation. This condition has been observed by Kowalevski (73) and Heider (44, 45, 46) in the case of *Hydrophilus*. The transverse boundaries not only extend over the middle plate from the invagination of which the lower layer arises, but laterally over the lateral plates which become the ectoderm of the germ-band. The transverse furrows arise due to the alternate thickening and thinning of the epithelium, the furrows correspond to the thin areas. Similar transverse zones have been observed by Wheeler (156) in *Doryphora* and by Graber (30) in *Lina*.

The appendages in most of the cases appear simultaneously with the segmentation. They are formed as evaginated sac-like structures of the ectoderm.

In *Mylabris* the segmentation of the germ-band becomes distinct even before it has attained its maximum length and the blastokinetic movements are over. After 85 hours of incubation the germ-band divides into an anterior broader region (Fig. 18, 19, 20, Plate 4) and a narrower posterior region (Fig. 17, Plate 4). The broader region is the protocephalon which is conspicuous on account of its large lateral lobes which give rise to the protocerebral segment. These lateral lobes do not enlarge and spread up the sides of the yolk in *Mylabris* to the extent as has been shown by various authors. The protocephalon will bear the labrum, the mouth, the eyes and the antennae. The narrower posterior part of the germ-band is the protocorm and gives rise to the gnathal or the jaw segments of the head, the thorax and the abdomen.

After 90 hours of development the protocorm also shows signs of segmentation and divides into (i) a broader anterior half and (ii) a narrow posterior half (Fig. 21, Plate 5). Thus the germ-band at this stage comprises three segments including the anterior-most protocephalon. The broader anterior half of the protocorm shows faint lines of further segmentations thus making it to appear as divided into six segments. Of these six segments the first three are the gnathal or the jaw segments comprising of the mandibular and first and second maxillary segments (Fig. 22, Plate 5; MND, MX_1, MX_2), while the remaining three segments give rise to the three thoracic segments (Fig. 22, Plate 5; THX_1, THX_2, THX_3). Now the germband upto this portion of the protocorm also shows slight lateral expansions and becomes so to say somewhat massive. The comparatively narrower posterior portion of the protocorm forms the abdomen which does not show any further indications of segmentation (Fig. 23, Plate 5; ABD).

The abdominal portion shows the first indications of segmentation at about 94 hours of incubation. First two abdominal segments (Fig. 24, Plate 5; ABD_1, ABD_2) are now well marked laying immediately behind the third thoracic segment. At this stage we can therefore count nine segments viz. protocephalon, three gnathal, three thoracic and two abdominal. The gnathal and the thoracic segments become more prominent. The remaining portion of the abdomen does not show futher segmentation. Further segmentation of the abdomen takes place after 100 hours of incubation (Fig. 27, 28, Plate 6) when faint indication of segmentation appear in the remaining portion of the abdomen. The segments are more pronounced in the anterior region than in the posterior region of the abdomen (Fig. 25, 26, 27, 28, Plate 6). The abdomen is finally divided into eleven segments, the last segment being the largest (Fig. 27, 28, Plate 6).

In the case of some insects such as *Gryllotalpa* and *Lepisma* Heymons (56) has observed the presence of a twelfth segment termed telson which bears the anus. Weismann (155) has observed in the case of *Carausius* a diminitive twelfth segment which becomes incorporated into the proctodaeum in the later embryonic development. The presence of a twelfth segment has also been observed by Strindberg (145) in *Eutermes* and in *Chaliocodoma* by Carriere (11) and in *Apis* by Nelson (101).

In *Mylabris* the proctodaeum arises not on the eleventh segment but on the contrary behind it. This condition has been observed in *Calendra* by Tiegs and Murray (150), in *Lina* by Graber (30) and in *Forficula* and *Periplaneta* by Heymons (55). According to Tiegs and Murray a terminal anus-bearing segment is proved for the insect abdomen, even though in many it has become reduced to vanishing point. The origin of the proctodaeal invagination, in *Mylabris*, behind the eleventh abdominal segment is in further support of the view that a terminal anus-bearing twelfth segment or the telson is present in *Mylabris* and has been reduced to vanishing point.

When the segmentation of the abdomen is taking place the gnathal or the jaw segments as well as the three thoracic segments become more pronounced and the mesoderm in this region also becomes segmentally constricted corresponding to the ectodermal segmentations. The mesoderm in this region is thinner than in the abdominal region and this is most probably due to the fact that the region is expanded laterally more here than in the abdomen. The mesoderm is very sparse in the protocephalon which is more expanded than the anterior half of the protocorm, the gnathal and the thoracic region. The mesoderm penetrates in the protocephalon only at a very late stage after the appendages are developed.

The antennary segment which assumes a pre-oral position at a later period of development is as a matter of fact post-oral in position. It only takes up its pre-oral position during the formation and consolidation of the head capsule. The antennary segment is located at the posterior-most margin of the protocephalic segment. The antennae arise as two small backwardly directed papillae from the postero-ventral region of the antennary segment. It is, however, in direct communication with the anterior-most end of the protocorm. The post-oral origin of the antennary segment has been observed in almost all the insects and this has been now accepted by all the previous authors, for *Hydrophilus*, *Meloe*, *Doryphora* and *Calendra*. The mandibular and the two maxillary segments are later drawn into the formation of the head into which they then become incorporated.

Thus the segmentation of the germ-band in *Mylabris* is first initiated in the anterior region and then proceeds backwards. The segmentation of the abdomen seems to be somewhat retarded and takes place only when the protocephalic, gnathal and the thoracic segments are well defined. The segmentations of the abdomen become well marked only after the cephalic and the thoracic appendages make their appearance.

1. THE APPENDAGES

The appendages can be divided into (1) the appendages of the head and (ii) the appendages of the thorax. The appendages develop as small hollow lateral evaginations of the ecotodermal walls situated laterally to the developing nerve cord.

The thoracic appendages are very conspicuous and extend backwards. The head appendages comprise the antennae, the labrum, the mandibles and the first and second maxillae. The second maxillae fuse together as the development proceeds and form the lower lip or the labium. The labrum forms the upper lip. Of the gnathal appendages the mandibles are the largest and strongest. The abdomen lacks appendages in *Mylabris*, although they have been observed in other Coleoptera like *Doryphora* by Wheeler (156), *Hydrophilus* by Graber (29, 32 , 33), *Meloe* by Nusbaum (104, 105), *Corynodes* and *Euryope* by Paterson (111, 112, 113) and *Calendra* by Tiegs and Murray (150) there are no appendages on the first abdominal segment.

(i) *The appendages of the head.*

The cephalic appendages develop from the head lobe and the three gnathal segments, the mandibular and the first and second maxillary (Fig. 22, Plate 5; MND, MX_1, MX_2).

The mandibles and the labrum appear somewhat earlier than the other cephalic appendages. The mandibles are the largest of all (Fig. 39, Plate 9; MND). There are no appendages pertaining to the intercalary segment, which is very degenerate and has only an inconspicuous mass of mesoderm associated with it.

The rudiments of the antennae which are to be regarded as the anteriormost pair of true limbs belonging to the cephalic region, arise as small backwardly directed papillae from the postero-ventral region of the protocephalic segment at the point where these pass into the mandibular segment (Fig. 26, Plate 6; ANT). The stomodaeal invagination (Fig. 25, Plate 6; ST) is situated, at this time, slightly in front of the origin of the antennae which thus appear to lie distinctly postoral in origin.

The intercalary segment merely shows a pair of obscure undulations, probably representing vestigial appendage rudiments (Fig. 25, Plate 6; INT.C). With the subsequent rapid growth of the anterior and lateral cephalic structures the antennae are carried upwards and forwards and eventually come to assume a pre-oral position.

The labrum arises a short distance in front of the stomodaeal invagination on the procephalic segment as a pair of ventral lobes (Fig. 34, Plate 8; LBR). The lateral margins of the lobes are in direct continuation with the protocerebral lobes. The two lobes come closer to each other and fuse together forming a single flap-like structure over-hanging the stomodaeal invagination. The fused basal portion gives rise to the clypeus while the distal portion forms the labrum proper. In the older embryo the labrum loses the bifid condition at the tip and can be seen as a single large lobe over-hanging the mouth opening.

After 150 hours of development the maxillary and the labial appendages become constricted into a large basal and a smaller distal part (Fig. 66, Plate 13; MX, LB). The distal lobe gives rise to the palp. This bilobed condition, it seems, arises by a transverse constriction of the appendage and not by any secondary addition of a basal part as described by Hirschler (59) in *Donacia*.

The mandibles become pointed at their distal ends and basally they are very broad. They also come to lie at the sides of the oral opening with their free pointed ends directed towards the mouth.

The maxillae come to occupy a postero-lateral position with regard to the mouth opening. Their distal ends are directed towards the mouth.

The second maxillae or the labial appendages meet in the mid-line behind the oral opening, their bases fuse together and the palps are directed towards the mouth. The mala arises as a blunt process from the basal half of the labial rudiment after the formation of the palp. In the later stages of development the palp becomes three jointed, the joints indicated by faint constrictions. The broad basal portion from which the mala and the palp arise forms the cardo.

The coelomic cavities of all these gnathal segments viz. the mandibular, first and second maxillary segments do not penetrate into the appendages. The mesoderm, however, penetrates as the appendages grow and bulge out in the form of loose mass. With the subsequent development of the appendages the mesodermal mass is also drawn by the ectodermal walls along with it with the result that a cavity appears in the appendages giving the impression that the coelomic cavities of the corresponding segments have also penetrated into the appendages. A detailed account of the coelomic cavities is given separately further on.

(ii) *The appendages of the thorax:*

The three thoracic appendages arise in a similar manner as the gnathal appendages. The rudiments of the thoracic appendages appear as small hollow outgrowths of the ectodermal wall and as development proceeds they become conspicuous and extend backwards. At 172 hours of incubation these appendages exhibit two faint constrictions, to give rise to three segments corresponding to the coxal, femoral and the tibial segments. The trochanter and the tarsus differentiate only at a very much later stage. The third pair of appendage soon extends nearly upto the seventh abdominal segment. The coelomic cavities of the thoracic segments do not penetrate into the cavities of the appendages.

2. ENDOSKELETON

In *Mylabris* the endoskeleton in the head region consists of the tentorium and the mandibular apodemes. The tentorium is represented by a transverse bar of chitin through the head capsule a little behind the circumoesophageal nerve commissure. The transverse bar of the tentorium extends from the base of one maxillad to the other (Fig. 130, Plate 25; TNT) . A pair of much thinner bars extend backwards from the base of each antenna and join with the transverse bar (Fig. 111, 112, Plate 22; TND)..

Three pairs of infoldings of the ectodermal walls of the head region have been observed by me in *Mylabris*. Paterson (113) has however recorded four such pairs of inpushings of the cephalic ectodermal wall in *Corynodes*, which she attributes to the antennary, mandibular, maxillary and the labial segments. Roonwal (127) has also observed four such pairs of invaginations in the cephalic region of which the first three arise respectively in front of, at the level of, behind the mandibles and the fourth pair arising behind the first maxillae.

According to him the first and the third pairs form the tentorium, the second forming the mandibular apodeme whereas the fourth pair gives rise to the salivary glands.

According to Paterson (111, 112, 113) the first pair of invagination pertaining to the antennary segment in *Europe* and *Corynodes* pass inwards and backwards to form the anterior arms of the tentorium. The second pair arises on the anterior margin of the mandibular segment, and pass inwards and downwards on each side of the stomadaeum to meet the antennary processes. The third pair arises on the maxillary segment, are strongly developed to form the mandibular apodeme for the attachment of the strong mandibular muscles. The last pair develops at the anterior border of the labial segment and forms the body of the tentorium.

As already stated in *Mylabris* only three pairs of cephalic invaginations arise. The first belongs to the antennary, the second pair arises on the maxillary segment (Fig. 103, Plate 20; TNT), and the third pair arises at the anterior border of the labial segment (Fig. 99, Plate 19; TNT). There is no pair at the anterior border of the mandibular segment.

The first pair arises dorsolaterally in the antennary segment and extends inwards, backwards and slightly downwards, eventually meeting with the main body of the tentorium at the sides of the stomodaeum.

The second pair of invagination arising on the maxillary segment is the most conspicuous and strongly developed of all the three pairs. Since the head is simultaneously undergoing a series of complicated changes involving the reduction in size of the post-oral intersegmental regions. Due to the reduction in size of the intersegmental regions the invaginations are slightly moved forwards and eventually come to lie at the posterior margin of the segments preceeding the one on which they were originally situated. Thus the second pair which actually arose on the maxillary segment comes to lie on the posterior part of the mandibular segment. This pair forms the mandibular apodeme for the attachment of the strong mandibular muscles (Fig. 99, Plate 19; Fig. 111, 112, Plate 22; MND. APD.)

The third pair arising on the labial segment also shifts its position due to the same reasons and eventually comes to lie at the posterior margin of the maxillary segment (Fig. 111, Plate 22; Fig. 130, Plate 25). The invaginations grow inwards towards each other pass over the sub-oesophageal ganglion, ventrally to the stomodaeum and meet to form the main body of the tentorium, to which the anterior tentorial arms are joined arising from the antennary segments (Fig. 111, 112, Plate 22; TNT, D. TNT.).

There is no further cephalic invagination behind the labial segment. Such invaginations have not been observed in any Coleoptera so far. In embryos of certain Lepidoptera these cephalic invaginations have however been observed, and give rise to the silk and hypostigmatic glands.

According to the observations of Tiegs and Murray (150) in *Calendra* the tentorium is formed by the fusion of only two pairs of tubular ingrowths of the ectoderm. Of these one pair arises at the bases of the antennae just anterior to the mandibles and the second pair arises at the hinder angle of the maxillae, between it and the labium. From the hinder angle of the mandibles there is no contribution of the ectodermal invagination. In this respect the development of the tentorium in *Calendra* resembles with that of *Hydrophilus* as observed by Heider (44, 45, 46), in *Formica* and *Chrysomela* by Strindberg (145, 146).

3. The tracheal system

The tracheal system, consisting of the spiracles, the stigmatic ingrowths and the trachea, arises as segmental ectodermal ingrowths in thorax and abdomen.

The paired invaginations of the ectoderm appear after the development of the appendages is well advanced. In the thorax these invaginations arise anterior and lateral to the appendages (Fig. 89, Plate 17; Fig. 120, Plate 23; SP) while in the abdominal region they arise close to the anterolateral margins of the abdominal segments (Fig. 85, Plate 16; Fig. 92, 93, Plate 18; Fig. 79, 81, Plate 15; Fig. 69, Plate 13; Fig. 114, Plate 22; Fig. 128, Plate 25; SP.)

As in most insects in *Mylabris* also the number of thoracic ectodermal invaginations is only two. Thus the first invagination is situated on the mesothoracic segment. There is no invagination of the ectoderm in the pro-thorax. The second thoracic invagination is situated on the metathorax (Fig. 89, Plate 17). In the abdominal segments only the first eight segments bear such ectodermal invaginations. The posterior abdominal segments have no such invaginations (Fig. 73, Plate 14; Fig. 88, Plate 17; Fig. 109, Plate 22).

Thus the number of tracheal invaginations in *Mylabris* is ten pairs, two of which belong to the thorax and the remaining eight to the abdominal region. This condition has been observed in majority of the embryos of Coleoptera by Graber (29, 32, 33), Strindberg (145, 146), Paterson (112). Nelson (101) has observed a similar condition in *Apis*. In *Pieris*, Eastham (19) observed ten pairs of spiracles but the thoracic spiracles are situated on the pro-and metathorax, the mesothorax is devoid of any spiracle.

According to Tiegs and Murray (150) in *Calendra* the number of spiracles is ten pairs but only the first seven abdominal segments have the spiracular invaginations while the pro-, meso-and metathorax has got each a pair of spiracular invaginations.

In *Corynodes*, however, Paterson (113) found slight invaginations on the ninth and tenth abdominal segments, in addition to the ten pairs from the mesothorax to the eighth abdominal segment. In *Doryphora*, Wheeler (156) has described vestigial stigmata on the prothorax and on the tenth and eleventh abdominal segments. In *Corynodes* Paterson (113) states that the spiracles on ninth and tenth abdominal segments are merely shallow inpushings of the lateral ectodermal wall. They are regarded as only rudimentary structures. Nine pairs of embryonic spiracles have been reported in *Donacia* and *Hydrophilus*.

The position and the number of the ectodermal pits in *Mylabris* have already been described. These pits arise as wide shallow inpushings of the ectodermal wall, but soon deepen and become very broad, ending blindly. From the blind end two diverticula are given off, one of which is short (Fig. 132, Plate 25; TR_1) and horizantal while the other is somewhat longer and is latero-dorsal proceeding towards the upper side along with the developing body wall. (Fig. 132, Plate 25; TR_2). The openings to the exterior which are at first very wide later on become very much reduced in size and form the spiracles. The above mentioned two branches subdivide repeatedly and thus the tracheal system is formed. The head and the prothorax receive its tracheal branches from the mesothoracic spiracle.

4. THE SENSORY ORGANS

The eye rudiment arises as a small disc-like area of a few ectodermal cells, which are larger than the neighbouring cells (Fig. 108, Plate 21; OP. PL). The broad and thick (Fig. 108, Plate 21; Fig. 98, 99, Plate 19; OP.PL) area invaginates rapidly, with the result that two cup-like depressions are formed on either side of the head capsule which has now consolidated to a considerable extent (Fig. 104, 105, Plate 20; EYE). The margins around the mouth of the cup-like depression push towards the centre of the depression, where they eventually meet (Fig. 103, Plate 20; Fig. 112, Plate 22; EYE). The cuticular covering the rudiment gradually becomes thick, smooth, convex and forms a bulging disc (Fig. 103, Plate 20; Fig. 112, Plate 22; LN). This bulging disc forms the chitinous lens. The layer of cells just underneath the lens constitutes the lenticular layer or the vitreous body (Fig. 103, Plate 20; Fig. 112, Plate 22; VT). The deeper layers of the cup-like depression form the retina (RT). The structure of the eye described above remains unaltered during the entire embryonic development.

5. THE SECONDARY DORSAL ORGAN AND DORSAL CLOSURE

After the rupture of the embryonic envelopes the term 'Secondary dorsal organ' is applied to the contracted serosa while in some cases the amnion. In *Mylabris* the amnion forms the provisional dorsal closure while the serosa contracts to form the tubular secondary dorsal organ. The secondary dorsal organ is well developed in many Coleoptera (*Hydrophilus*, *Donacia*, *Tenebrio*, *Meloe* and *Dytiscus*).

With the rupture of the embryonic envelopes viz. the serosa and amnion both of which are thrown upwards. The serosa contracts on the dorsal side opposite to the developing embryo in the form of a arc of compact cells. The serosa thus contracted forms the secondary dorsal organ (Fig. 114, Plate 22; Fig. 118, Plate 23; S.D.O.). The ectoderm of the developing embryo remains connected with this organ through a very thin membranous amnion on either side (Fig. 114, 115, Plate 22; Fig. 118, Plate 23; AMN). The secondary dorsal organ extends from the posterior end (Fig. 114, Plate 22; S. D. O). nearly upto first or second thoracic segments (Fig. 118, Plate 23; S.D.O.).

With the upward development of the lateral body-wall of the embryo there is an inward push from either side on the secondary dorsal organ. The result of this pushing, and most probably due to the absorption of the yolk lying immediately underneath the organ, the secondary dorsal organ collapses inwards. As a result, a narrow groove appears in it (Fig. 117, 119, Plate 23; S. D. O.).

The mouth of the groove closes and the secondary dorsal organ assumes a tubular structure with a narrow lumen in it. The groove closes from behind forwards. Figure 117 and 122 of plate 23 represent the secondary dorsal organ of which the later is from the posterior region while the former is from the anterior region. By this time the length of the secondary dorsal organ is also reduced.

When the definitive dorsal wall of the embryo is fully developed (Fig. 123, Plate 24; D. D. CLO), the secondary dorsal organ sinks in the yolk and undergoes degeneration. The degenerating cells lose their epithelial connection and are absorbed into the intestinal canal with the rest of the yolk (Fig. 128, Plate 25; S. D. O).

The dorsal parts of the cephalic region of the embryo develop independently which is formed by the bending over dorsally and the backward extension of the cephalic lobes as well as the protocephalon (Fig. 87, 90, Plate 17; HD.L). The consolidation and the dorsal closure of the head takes place much earlier than the formation of the secondary dorsal organ.

As the germ-band grows considerably in breadth, its lateral margins move up dorsally over the yolk. By this the yolk comes to lie entirely within the embryo and finally fills the lumen of the mid-gut (Fig. 123, Plate 24; YK).

ALIMENTARY CANAL

The alimentary canal of insects can be divided into three primary divisions, the fore-, mid- and hind-gut. The rudiments of these appear very early in the embryo. The fore-and hind-gut arise as invaginations of the ectoderm. The fore-gut appears in the anterior region and is called the stomodaeum while the hind-gut appears in the posterior region and is called the proctodaeum. As a general rule the stomodaeum appears earlier than the proctodaeum. In a number of cases, however, the proctodaeum appears first as has been observed in the head louse, the flour moth *Ephestia* and in some *Chrysomelids* among Coleoptera. From the stomodaeal invagination originate the oesophagus, the proventriculus as well as the salivary glands while the proctodaeal invagination gives rise to the ileum, colon, rectum, the rectal glands and the Malpighian tubules. Of these the Malpighian tubules arise as evaginations from the blind end of proctodaeum. Of the recent writers only Henson (51), in the case of *Pieris brassicae*, has shown that the Malpighian tubules are endodermal in origin.

(i) EARLY DEVELOPMENT OF THE ALIMENTARY CANAL IN *MYLABRIS*

The stomodaeum makes its appearance first after 100 hours of incubation (Fig. 25, Plate 6; ST), after the blastokinetic movements are over. By the time the stomodaeal invagination appears the gnathal segments are already distinct (Fig. 25, Plate 6; MND, MX_1, MX_2). The labrum however appears only a little later while the stomodeal invagination is still very feeble. The proctodaeal invagination has not yet appeared (Fig. 27, 28, Plate 6).

At the blind end of the stomodaeal invagination there is so far no cell proliferation (Fig. 25, Plate 6; ST) to give rise to the anterior or stomodaeal component of mid-gut. At the tip of the inner layer of the invagination a small cluster of the mesodermal cells (Fig. 25 Plate 6; MSD) must not be mistaken for anterior endoderm rudiment. A very similar case of the heaping of the mesodermal cells has been observed in *Calendra* by Tiegs and Murray (150) who hold the view that the heap of the cells is not the anterior endoderm rudiment. The ectodermal invagination pushes inwards the mass of mesodermal cells and thus gives an impression of endodermal heaping. With formation of the stomodaeum the mesodermal cells are separated on either side of the invagination and assume pre- and post-oral positions. According to Tiegs and Murray (150) the ectoderm behind the stomodaeal invagination is unusually thin in *Calendra*. This is, however, not the case in *Mylabris*. Though somewhat thick before invagination, the ectoderm in front and immediately behind it is more or less of uniform thickness (Fig. 25, Plate 6).

The stomodaeal invagination becomes deeper and assumes a somewhat hemispherical shape after 106 hours of incubation (Fig. 34, Plate 8; ST). The cells of the anterior endodermal rudiments may be distinguished at this stage (Fig. 34, Plate 8; A. END.R).

The proctodaeum developes as a wide dorso-ventrally compressed invagination of the ectoderm into the yolk from the hinder-most end of the germ-band after 112 hours of incubation (Fig. 63, 64, Plate 12; PCT). Since the germ-band does not reach the tip of the egg posteriorly its position is more or less vertical. Its ventral wall is somewhat thicker than the dorsal wall, which is in direct continuation with the amnion (Fig. 63, 64, Plate 12; AMN) and is very thin. As it is often not easy to demarcate the limits between the proctodaeal and amniotic cavities at this stage some authors speak of the cavity thus formed as proctodaeal-amniotic cavity. After 124 hours of incubation however the proctodaeum becomes well defined. The dorsal wall which was hitherto thin becomes thick. The proctodaeum which was vertical in position becomes now more or less horizantal and its blind end becomes directed towards the anterior pole of the egg (Fig. 42, Plate 9; PCT). The dorso-ventrally compressed cavity now becomes somewhat tubular. At the thick blind end may now be seen the cells which constitute the posterior rudiment of the mid-gut or the posterior endoderm rudiments (Fig. 42, Plate 9; P. END. R). The lumen of the proctodaeum which can now be sharply distinguished from the amniotic cavity, is relatively narrow at the blind end.

The exact nature of the origin of mid-gut has remained largely uncertain. The mid-gut epithelium is derived from the yolk cells in *Lepisma* and *Campodea* by Heymons.

The mid-gut epithelium has also been derived from the stomodaeum and the proctodaeum (hence ectodermal) by Lecaillon (86), Deegner (15), Friederichs (22), Mansour (90, 94) and Tiegs and Murray (150) on Coleoptera.

Roonwal (126, 127) also holds this view for *Locusta*. My observations on the origin of the mid-gut epithelium in Mylabris agree with the views of these workers.

The mid-gut cells have also been described as arising either by delamination, or invagination, or inward proliferation from the outer layer, completely independent of the proctodaeum and stomodaeum in Hymenoptera by Strindberg (145, 146), in *Carausius* by Wiesmann (155), in *Calendra* by Inkmann (64) and in *Corynodes* by Paterson (113). In all such cases the anterior and posterior endodermal rudiments are said not to occur at all.

THE DEVELOPMENT OF MID-GUT IN MYLABRIS

As has already mentioned, the mid-gut is derived from the anterior or stomodaeal endodermal rudiment and the posterior or proctodaeal endodermal rudiment. The cells of the anterior endodermal rudiment become differentiated after 106 hours of incubation. The endodermal cells are restricted only in the region just above the blind end of the stomodaeum (Fig. 34, Plate 8; A. END. R.) After 112 hours of incubation a few of these cells can be seen upto the level of the first maxillary segment (Fig. 43, Plate 9; MG.EPT), where they appear as a pair of narrow lateral bands lying on the mesodermal mass next to the yolk. In the anterior region just above the stomodaeal invagination they appear as a broad sheet of cells under the yolk. These cells are somewhat larger than the mesodermal cells. Since the coelomic sacs are formed at a very late stage in *Mylabris* and even before such sacs develop the formation of the mid-gut epithelial cells by the local differentiation of cells from these sacs is very doubtful. Moreover before the coelomic sacs are fomred the mid-gut ribbons arising from the anterior and posterior endodermal rudiments fuse together giving continuous ribbons on either side right from the stomodaeum upto the proctodaeum. Thus the cells of the mid-gut have migrated back from the anterior endoderm rudiments and forward migration of these cells takes place from the posterior endoderm rudiment. The formation of the mid-gut cells by the local differentiation of the coelomic sacs does not seem to be possible.

The proctodaeal or posterior endoderm rudiment appears much later than the anterior endodermal rudiment, which has already grown back upto the end of the second maxillary segment (118 hours of incubation; Fig. 45 Plate 10; MG. EPT). The blind end of the proctodaeum becomes wider and curves (Fig. 96 Plate 18; PCT) over the mesodermal mass lying at the hinder part of the germ-band. The posterior endoderm rudiment appears as a mass of cells crowded at the blind end of the proctodaeum. At about 118 hours of incubation the posterior endoderm rudiment grows out into two lateral strands of cells in a similar fashion as the two lateral strands growing out from the anterior endoderm rudiment. The subsequent growth of this rudiment is comparatively slower than the anterior rudiment.

The lateral strands growing from the posterior endoderm rudiment are however much more conspicuous than their anterior counterpart. The posterior ribbons are since the beginning at some distance from the mesodermal mass, though they lie over the mesodermal mass cutting it completely away from the yolk. The anterior ribbons lie very close over the mesodermal mass and are also thinner than the posterior ones.

The lateral strands from the anterior endoderm rudiment grow backwards in between the yolk and the mesodermal mass while those from the posterior rudiment grow forward in a similar fashion till they meet each other.

(ii) LATER DEVELOPMENT OF THE ALIMENTARY CANAL.

THE STOMODAEUM

The stomodaeum is a short blind tubular ectodermal invagination in a plane vertical to the germ-band. It afterwards assumes a more or less cylindrical form with a wide lumen projecting into the yolk (Fig. 66, 68 Plate 13; ST). As the development of the embryo advances the stomodaeum assumes the shape of an elongated tube ending blindly, its walls being composed of densely packed more or less cylindrical cells. In a fairly advanced stage the opening of the stomodaeum to the outside becomes constricted. The dorsal wall becomes thicker than the ventral and the blindly ending wall (Fig. 71 Plate 13; ST). The thickening of the dorsal wall of the stomodaeum is most probably due to the formation of the frontal ganglion and the stomatogastric nervous system to be described separately under 'Nervous System.'

After the formation of the frontal ganglion the dorsal wall of the stomodaeum becomes thin, but it is thicker than the ventral wall (Fig. 77 Plate 14; Fig. 80, Plate 15; Fig. 83, Plate 16; ST). After 194 hours of incubaion the stomodaeal tube becomes very much elongated (Fig 83, Plate 16; ST). Its blind end now becomes enlarged with the wall reduced to a thin membrane, forming a sort of partition between the lumen of the stomadaeum and the endodermal cells which are closely heaped up outside.

The stomodaeal musculature seems ot be derived mainly from the pre-oral (Fig. 34, Plate 8; MSD) and partly also from the post-oral masses of mesoderm (Fig. 36, Plate 8; MSD). The two mesodermal masses i.e. the pre-and post-oral completely invest the stomodaeum. A fuller account of the formation of the musculature is dealt separately.

Just before the completion of the mid-gut epithelium the hinder end of the stomodaeum dilates further and bulges out (Fig. 131, Pate 25; ST). The anterior portion becomes narrow and tubular. The walls are now composed of thin flattened cells. The dilated portion is the proventriculus (Fig. 131, Plate 25; P. VNT), while the narrow tubular portion constitutes the oesophagus (Fig. 131, Plate 25; OES), the opening to the exterior being the mouth. By this time the stomodaeum assumes a horizantal position. The portion of the stomodaeum immediately behind the mouth opening and in front of the oesophagus is the pharynx (Fig. 131, Plate 25; PHX).

The proventriculus opens into the mid-gut and at the entrance the oesophageal valves can be seen as small projections (Fig. 131, Plate 25; OES. V). In the later stages of development the stomodaeum appears folded in cross-sections with muscles surrounding it (Fig. 111, Plate 22; Fig. 121, Plate 23; ST).

THE PROCTODAEUM

The proctodaeum has so far been a tubular organ in a horizantal position along the long axis of the germ-band with almost uniformly thick wall (Fig. 86, Plate 16; Fig. 91, Plate 17; PCT). The mid-gut that is forming as a pair of lateral ribbon-like outgrowths, is continuous with the ventral wall of the proctodaeum. After its differentiation the posterior endoderm rudiment is found in the lower part of the blind end of the proctodaeum. No internal opening of the proctodaeal lumen, described in *Calendra* by Tiegs and Murray (150) has been found by me.

About the 172nd hour of incubation finds the proctodaeum considerably elongated. Its blind end becomes enlarged, thin and forms a sort of partition between the lumen of the proctodaeum and the posterior endodermal rudiment (Fig. 75, Plate 14; PCT). At the place where this thin end passes into the thicker proctodaeal wall two small pits represent evaginations of the ectodermal wall, as the rudiments of the Malpighian tubules (Fig. 75 Plate 14; MT.R). There seems to be therefore no doubt about the ectodermal origin of the Malpighian tubules in this insect. The endoderm does not play any part in the development of the tubules, the thin wall of the blind end of the proctodaeum completely cuts away the endodermal rudiment from the rudiments of the tubules.

At this stage the proctodaeum curves somewhat ventrally, with its opening being slightly constricted. Dense clusters of mesoderm cells occuring on the sides of the proctodaeum (Fig. 73, 75 Plate 14; MSD) contribute to the formation of the muscles of the proctodaeum. This mesoderm cell mass is derived mostly from the mesoderm of the last abdominal segment. These cells spread forward along the walls of the proctodaeum and envelope it along its whole length. As a result of this association very little of the free mesoderm may be found in the last abdominal segment (Fig. 75 Plate 14; Fig. 91 Plate 17; MSD). The Malpighian tubules grow into this mass before its organisation into an investing sheath for the proctodaeum.

During the subsequent development the proctodaeum elongates rapidly (Fig. 107, Plate 21; PCT). The cells of the proctodaeal wall also enlarge, assume a more or less flat shape. The proctodaeum as a whole becomes looped.

The outer proctodaeal opening or anus shifts to the ventral side (Fig. 91, Plate 17; Fig. 109, Plate 21; PCT). The anterior proctodaeal end is connected with the mid-gut, which is now fully formed. The proctodaeal opening into the mid-gut is gaurded by proctodaeal valves which are similar to the stomodaeal valves.

Somewhat behind the junction of the mid and hind-gut the Malpighian tubules open; this opening is situated a little behind the proctodaeal valves (Fig. 101, Plate No. 19; MT). The Malpighian tubules are also invested around by the mesoderm forming a sheath around them (Fig. 91, Plate 17; Fig. 92, Plate 18; Fig. 101, Plate 19; Fig. 102, Plate 20; Fig. 107, Plate 21; MSD, MT. R, MT). The mesoderm can be distinguished into a thick sheath investing the proctodaeum and a comparatively thin sheath investing the Malpighian tubules. This mesoderm arranges itself at the later stages of development around each Malpighian tubule in the form of a very thin sheath.

The thin ectodermal partition at the blind end of the proctodaeum ruptures and communication between the hind-gut and mid-gut is established only when the embryo is fully developed. The partition between the stomodaeum and the mid-gut also ruptures (Fig. 131, Plate 25; OES. V), so that the alimentary canal is complete.

The looped proctodaeum becomes differentiated after the mid-gut epithelium is complete into a somewhat dilated ileum a narrow colon and the rectum. The diameter of the rectum is the greatest of all the three parts. Just before hatching, the lining of the rectum projects into its lumen in somewhat longitudinal folds called rectal glands.

THE MID-GUT

With the growth of the brain and the muscles of the head, the yolk, which has now diminished in quantity to a great extent recedes into the thoracic region (Fig. 82, 83, Plate 16; Fig. 90, Plate 17).

The lateral bands of the mid-gut epithelium multiply and by the time the coelomic sacs are well differentiated, spread downwards from the two sides under the yolk and fuse together ventrally. The mid-gut epithelium is thus already completed on the lower side (Fig. 74 Plate 18; MG. EPT). After the coelomic sacs are differentiated the splanchnic (Fig. 85, 86 Plate 16; Fig. 89, Plate 17; Fig. 94, Plate 18; SPL. MSD) or the inner layer of the mesoderm becomes closely associated with the mid-gut. The splan chnic meso derm also spreads with the mid-gut epithelium and the splanchnic mesoderm can be easily recognised by a distinct line of demarcation between them.

Before the mid-gut lateral bands spread, they consist of closely packed cells (Fig. 89, Plate 17; MG. EPT), but as the epithelum spreads, the cells separate and form the simple epithelium of the mid-gut (Fig. 94, Plate 18; MG. EPT). The mid-gut cells are recognized by their hyaline cytoplasm.

When the lateral body-wall of the embryo enlarges upwards the mid-gut also starts spreading with it. The advancing epithelium from both the sides fuse together below the heart, with the result that the yolk is completely enclosed by the mid-gut epithelium cells. At the same time a pre-oral mass of cells (Fig. 82, 83, Plate 16; PR.O.MG.CL) also spread forward and upwards and fuse with the dorsal wall of the mid-gut.

MALPIGHIAN TUBULES

The Malpighian tubules arise as ectodermal evagination of the proctodaeal wall (Fig. 75, Plate 14;). They are not endodermal is shown by the fact that their origin is far back from the posterior endodermal rudiment and moreover that a thik ectodermal septum of the blind end of the proctodaeum separates their place of origin and the anterior endodermal rudiment. The Malpighian tubule rudiments push their way out into the mesoderm surrounding the proctodaeum (Fig. 84, Plate 16, MT.R). In the beginning the Malpighian tubules curve backward. In fairly advanced stages the tubules become very long and reach nearly upto the last abdominal segment along the sides of the proctodaeum (Fig. 101 Plate 19; Fig. 102, Plate 20; Fig. 107, Plate 21; MT). The tubules are enclosed in the mesodermal mass surrounding the proctodaeum through which they push their way.

The number of the Malpighian tubules in *Mylabris* is six, three on either side (Fig. 88, Plate 17; MT). The mesoderm surrounding the tubules later forms a thin envelope round each tubule. The tubules open into the proctodaeum through a single oepning as can be seen in transverse sections passing through that region (Fig. 88, Plate 17; Fig. 92, Plate 18); each tubule does not open separately into the proctodaeum and has a narrow lumen from the very beginning.

The Malpighian tubules appear in majority of cases, only after the development of the proctodaeum is fairly advanced but in certain Hymenoptera (*Apis* and *Chalicodoma*) they are reported to appear before the proctodaeum developes as invagination of the germ-band. Only later they shift with the developing proctodaeum into the interior of the embryo.

MESODERM AND ITS DERIVATIVES

MESODERM

At the same time when the insinking of the germ-band starts the so-called gastrular groove becomes apparent from the posterior end forward along its mid-ventral line (Fig. 3, Plate 1; GST.GR). Somewhat later the anterior end of the germ-band also shows a shallow groove (Fig. 1, Plate 1; GST. GR). This shallow anterior groove extends backwards and the posterior groove extends forwards until the two grooves meet. The gastrular groove is thus formed along the entire length of the germ-band. Active cell proliferation can be observed at the posterior end of the groove. The proliferating cells give rise to the inner or lower layer (Fig. 1, 2, 3, 4, 5 Plate 1; IN.LY). With the progress of cell proliferation at the posterior as well as the anterior end the gastrular groove becomes obliterated.

The inner layer thus formed soon spreads evenly over the outer layer of the germ band as a solid band of cells. (Fig. 6, 7, 8, 9, Plate 2; IN. LY). The outer layer of the germ band constitutes the ectoderm (Fig. 25, 26, 27, 28 Plate 6; ECT), while the inner layer forms the mesoderm Fig. 26, 27, 28 Plate 6; MSD). After the overlying ectoderm becomes segmented, the mesoderm also becomes constricted segmentally. The mesoderm is thicker at the sides and thin in the middle. In the intersegmental zone the mesoderm is very much reduced due to the constrictions of the mesodermal mass indicating its segmentation.

In the cephalic (Fig. 60, 61, 62 Plate No. 12; Fig. 52, 54, 56 Plate 11; MSD) and gnathal segments (Fig. 34, 36, 37, Plate 8; MSD) the mesoderm layer is thinner than in the thorax and abdomen (Fig. 33, 35, Plate 8; MSD). This is perhaps due to the fact that the gnathal and cephalic regions expand rapidly sideways (Fig. 34, 36, 37, Plate 8; Fig. 39, 43, 44, Plate 9; Fig. 52, 54, 56, Plate 11) stretching the mesoderm. The appendages in the gnathal region develop cavities in them and a part of the mesoderm is also drawn into these cavities (Fig. 60, Plate 12; MND, MX_1, MX_2). The mesoderm of the appendages is solid at first but as development proceeds it becomes loose clumps of cells (Fig. 66, 68, Plate 13; Fig. 74, Plate 14; MND, MX_1, MX_2). These loose clumps of cells later migrate to the walls of the appendages and become arranged into simple linings for the appendages (Fig. 71. Plate 13; LG_1, LG_2; Fig. 72, Plate 14; MND, MX. LB, LG_1, LG_2; MSD). Closed sacs, however, do not form and the cavities enclosed in the appendages should not be confused with the penetration of the coelomic sacs,in the appendages, which develop in the segmental mesoderm.

When the stomodaeal invagination pushes inwards a heap of mesoderm cells or the pre-oral mesoderm (Fig. 25, Plate 6; PR.O.MSD) can be seen in front of it. It has its origin in the post-oral region. This mass of mesoderm should not, however, be confused with the anterior endodermal rudiment and it plays no part in the formation of the mid-gut epithelium. At this time there is moreover no differentiation of the anterior endodermal rudiment, which really arises at a much later stage. This condition can be seen in the 100 hour stage of development in the longitudinal sections.

As development proceeds and the stomodaeal invagination becomes well marked and deeper, the anterior endodermal rudiment becomes apparent. The pre-oral mesodermal mass undergoes acitive division. The cells spread forward round the stomodaeal invagination in the form of two thin sheets laterally along the inner side of the ectoderm of the protocephalic segment. The two lateral bands of mesoderm of the protocephalic segment are in continuation with each other in front of the stomodaeal invagination in the form of a transverse band of cells. The stomodaeum is thus completely encircled by the mesodermal cells.

The cavity of the labrum is now invaded by cells migrating from the mesoderm laying in front of the stomodaeal invagination.

The pre-oral mesoderm mass forms a consolidated layer in the protocephalic segments at about 112 hours of incubation. It spreads out also laterally as a layer of scattered cells. This can be easily seen in the longitudinal sections passing through the lateral regions of the protocephalic segment at 130 hours of developmental stage (Fig. 61, 62, Plate 12; MSD, HD. L).

The mesoderm, which becomes associated with the antennae, is very conspicuous, with the subsequent development of the head capsule and with its lateral expansions the antennae are also crarried forwards and now occupy a pre-oral position (Fig. 54 Plate 11; Fig. 67, 70 Plate 13; Fig. 74, 76, 77, Plate 14; Fig. 87, Plate 17; ANT).

COELOMIC SACS

The consolidation of mesoderm in the segments is soon followed by the development of the coelomic sacs, as small cavities in the lateral mesoderm.

The appearance of coelomic sacs in *Mylabris* proceeds from the labial to the ninth abdominal segment. There is no coelomic sac in the tenth abdominal segment. The mesoderm of the mandibles and the maxillary segments fail to show coelomic cavities (Fig. 67 Plate 13; MND, MX). There is no coelomic cavity in the labrum (Fig. 68 Plate 13; LBR).

In the procephalic segment only one pair of coelomic sacs appear and these are the antennary coelomic sacs (Fig. 67, 70 Plate 13; ANT. COE. S) which do not, however, penetrate the cavities of the antennae and are confined to the bases of antennae. The antennary coelomic sacs are the smallest and appear much later than those of other segments (150 hours of incubation).

In *Mylabris* the paired preantennal appendages are absent, hence the absence of preantennal coelomic sacs. Hirshler (59) has observed the absence of antennal coelomic sacs in the beetle *Donacia* which is the only exception recorded among the insects where sacs normally occur. Tiegs and Murray (150) have gone to the extent of saying that the presence of the second antennal or premandibular coelomic sacs which Hirschler found in *Donacia* are in reality the antennal sacs. The presence of second antennal coelomic sacs has been observed in *Locusta* by Roonwal (125, 126), in Chrysomelid beetle, *Euryope* by Paterson (111), 112) and in *Calendra callosa* by Wray (164).

In *Corynodes*, Paterson (113) has observed that the antennary mesoderm shows no characteristic somite formation and no spaces in it. It simply forms a fairly uniform layer which gives rise to the muscles passing into the cavity of the antennae. Part of it also extends dorsally and after passing dorsolaterally between the brain and the stomodaeum, develops into the anterior aorta. The aorta in *Euryope*, according to the same author, develops from the intercalary segment.

The inconspicuous premandibular or the intercalary mesoderm does not give rise to any coelomic cavities in *Mylabris*. The coelomic sacs in *Mylabris* present considerable similarities to those observed in the higher orders of insects. The presence of large, trilobed cavities, which even extend into the appendages have been described for the more generalized forms such as Orthoptera by various authors and in *Eutermes* by Strindberg (145). Such a condition does not exist in *Mylabris*, but this species agrees with the account of the number and manner of formation of the coelomic sacs in *Calendra* by Tiegs and Murray (150).

The occurrence of the coelomic sacs in *Mylabris* from the labial to the ninth abdominal segment agrees well with Hirschler's (59) observations in *Donacia* and also with those of Tiegs and Murray's (150) observations in *Calendra*. According to Hirschler the intercalary coelome is well developed in the former species and the cephalic aorta is said to arise from it, while the antennary coelome is absent. The antennary coelome seems to be absent in *Hydrophilus* also. In *Mylabris* the antennary coelome is present and the aorta arises from it. The origin of the cephalic aorta from the antennary coelome has been observed in *Calendra* also.

The narrow clefts in the segmental mesoderm enlarge and form cavities in the mesoderm (Fig. 69, Plate 13; Fig. 73, Plate 14; Fig. 79, 81. Plate 15; COE. S). The splitting of the mesoderm is first initiated at the lateral edges and then proceeds inwards. The result of the formation of the coelomic cavities is the formation of two lamellation of the mesoderm. The inner lamella is in close association with the mid-gut ribbons of either side and forms the splanchnic mesoderm (Fig. 69 Plate 13; Fig. 79, 81, Plate 15; SPL. MSD) which is very thin This layer of meoderms gives rise to the muscles of the mid-gut. The splanchnic mesoderm spreads along the mid-gut layer and is seen always in close association with it though the two layers can be easily distinguished from one another.

The outer lamella of the mesoderm is thick and lies in close contact with the ectoderm to form the somatic mesoderm (Fig. 69, Plate 13; Fig. 79, 81, Plate 15; SM.MSD). The muscles of the body wall, the abdominal muscles as well as the muscles of the thorax are derived from this layer. The inner wall of the somatic mesoderm breaks up in the form of loose cells that give rise to fat body (Fig. 79, 81, Plate 15; Fig. 85, Plate 16; F. B.). These cells migrate within the coelomic cavity and completely obliterate the coelomic cavity itself (Fig. 79, Plate 15; F. B.)

The vascular tissue is differentiated from the place where the splanchnic and the somatic mesoderm meet dorso-laterally (Fig. 85, Plate 16; Fig. 89, Plate 17; Fig. 93, 94, Plate 18; CRD).

The coelomic sacs are more or less oval and slightly elongated in the labial and thoracic segments but more or less spherical in the abdomen. In the beginning when the coelomic sacs are well developed, the cavities of the sacs are separated from each other in the intersegmental regions by somewhat stout septum. In the stage representing 172 hours of development these septa can be seen very much reduced and have become extremely thin (Fig.

81, Plate 15). During the subsequent development these septa disappear and a communication is established between the cavities of the successive segments through narrow but well defined channels in the intersegmental regions. Thus the coelomic sacs form a continuous pair of tubes running on either side from the labial upto the ninth segment of the abdomen. Such a condition is well known for Orthoptera and Dermaptera. Among Coleoptera, Hirschler (59) does not describe such a condition in *Donacia.* In *Melolantha* and *Lina*, Graber (30, 31) has observed such a condition, while Heider (44, 45, 46) has also observed the same in *Hydrophilus.* In *Calendra*, Tiegs and Murray (150) have observed a similar condition.

SUB-OESOPHAGEAL BODIES

The development of sub-oesophageal bodies is of particular interest since they are said to arise in two distinct methods. In Orthoptera, Wheeler (158), Heymons (55) and Wiesmann (155), in Isoptera, Strindberg (145) and *Pieris* by Eastham (18, 19) and Wiesmann (155) the suboesophageal bodies are said to arise from the mesoderm of the premndibular or the inter-calary segments. An entirely different process is described in Orthoptera by Nausbaum (106), in *Donacia* Hirschler (59), in Lepidoptera by Schwangart (133, 134), Hirschler (57, 58, 60) and Johannsen (66,67). According to these authors the sub-oesophageal bodies are said to arise from the mid-gut. In *Stenobothrus* and *Locusta* the origin of the sub-oesophageal bodies is attributed to the mesoderm of the mandibular segment. In *Calendra oryzae* according to Tiegs and Murray (150) it is derived from the mesoderm of the intercalary segment, but becomes secondarily attached to the mid-gut wall and has the appearance of developing from it.

The formation of the sub-oesophageal bodies in *Mylabris* afford further confirmation of the observations of Tiegs and Murray for *Calendra.* In longitudinal sections passing through the anterior region of the embryo after 150 hours of incubation the sub-oesophageal bodies (Fig. 71, Plate 13; SBO.B) can be distinctly seen when they differentiate from the mesoderm. The position occupied by them is somewhat anterior to the mandibles, very close to the stomodaeum. The mesoderm in the pre-mandibular or the inter-calary segment is now left very little while the mesoderm in the mandibular segment has not been affected much. Moreover the position of sub-oesophageal bodies is not in close contact with the mid-gut wall which is well developed by this time. If a comparison is made regarding the position of the sub-oesphageal bodies in a longitudinal section of the anterior end of the embryo after 172 hours of incubation it can be seen that their position has now shifted and they are in close contact with the mid-gut wall (Fig. 80, Plate 15; SBO.B)

All the authors are so far in agreement regarding the position occupied by these bodies which is in close contact with the mid-gut wall. There seems to be doubt in assuming that after the differentiation of the sub-oesophageal bodies they become separated from the mid-gut wall and during the subsequent development they again change their position and attach themselves to the mid-gut wall.

The cells of the sub-oesophageal bodies can be distinguished by their large size and their cytoplasm being faintly granulated. They also show a few cavities in them.

Although in the later stage i.e. after 172 hours of incubation a few blood cells (Fig. 80, Plate 15; BL.CL) are seen near the sub-oesophageal bodies when these are located in close contact with the mid-gut wall, the origin of these cells from the sub-oesophageal bodies can not be said with certainty.

BLOOD VASCULAR SYSTEM

(i) *The Haemocoele:*

The haemocoele developes as the epinural sinus first (Fig. 69, Plate 13; EP.SN). The mesoderm immediately overlying the nerve cord is withdrawn to the sides (Fig. 69, Plate 13; Fig. 85, Plate 16; S.S. MSD) and becomes incorporated in the main segmental mass of the mesoderm. When the fat becomes well differentiated the lateral blood sinus merges below into the epinural sinus (Fig. 85, Plate 16). When lateral sinuses merge into one another above the mid-gut after the dorsal closure of the embryo is brought about the gut also is enclosed within the haemocoele (Fig. 125, 126, Plate 24).

When these developments are taking place the nerve cord in the mean time separates off from the ectoderm and thus it also comes to lie within the haemocoelic space.

The proctodaeum also separates from the fat body during the subsequent development and the haemocoele extends upto the last abdominal segment (204 hour stage) (Fig. 88, Plate 17; HMC).

With the enlargement of the head capsule and the subsequent development of the stomodaeal invagination the yolk is pushed back well into the thorax. As a result of this a very conspicuous and well defined space appears in the head (Fig. 70, Plate 13; HMC) and is continuous behind with the haemocoele of the thorax. The haemocoele of the head region enlarges further and accommodates the brain (Fig. 90, Plate 17; HMC, BR).

(ii) *The Blood cells.*

These arise from the unsegmented median mesoderm which form a sort of bridge in the median region, between the segmental mesodermal mass (Fig. 69, Plate 13; BL.CL). The blood cells are clear hyaline and with vacuolated cytoplasm. These are first to be seen in the thoracic region but later they can be seen scattered everywhere in the body.

THE DORSAL BLOOD VESSEL

The dorsal blood vessel of *Mylabris* consists of three main parts (i) the heart with the alary muscles (ii) the aorta and (iii) the cephalic aorta.

The heart and the aorta are derived from the dorsolateral walls of the coelomic sacs. Thus all the coelomic sacs from the ninth abdominal to the labial segment contribute in their formation. The contribution of the gnathal mesoderm anterior to the labial segment towards the formation of the heart and aorta is doubtful.

The differentiation of the cardioblasts (Fig. 85, Plate 16; Fig. 89, Plate 17; Fig. 93, Plate 18; CRD), in the dorso-lateral walls of the coelomic sacs where the splanchnic and the somatic mesoderm meet, takes place at a very later stage of development (194 hours). According to Tiegs and Murray (150) the same is the condition with regard to *Calendra*.

When the development has proceeded in a well advanced stage the somatic and the splanchnic layers of the mesoderm appear to be separated from one another and a stretched, thin and cresentic membrane can be seen in between the two layers of the mesoderm. After 204 hours of incubation (Fig. 89, Plate 17; CRD) the cardioblasts differentiate as a few enlarged cells towards the yolk side of the thin membrane. Some mesoderm is also attached on the convexity of the cresentic membrane on the inner side. This whole structure constitutes the heart anlagen. This mesodermal mass later differentiates into the alary muscles, pericardial and paracardial rudiments.

When the lateral body wall spreads upwards over the yolk the heart anlagen of either side is also carried towards the dorsal surface of the embryo where they eventually meet (Fig. 126, Plate 24; HT).

Throughout the development the heart rudiments have a loose connection with the splanchnic mesoderm. Later on when the heart rudiments are well over the yolk on the dorsal side this connection is lost. The formation of the heart and the subsequent differentiation of the various associated structures takes place at a very late stage.

The mesodermal mass which accompanies the cardioblasts forms the muscles of the heart, the alary muscles (Fig. 126 Plate 24; AL. MSL).

The cephalic aorta arises by the fusion of the coelomic sacs of the antennary segments.

THE MUSCULAR SYSTEM

(i) *Muscles of the head:*

The mesoderm in association with the antennal segment gives rise to the flexor and the extensor muscles of the antennae. Although the mesodermal mass penetrates inside the antennal cavities (Fig. 76, 77, Plate 14; Fig. 87, Plate 17; Fig. 97, Plate 18; ANT) yet it does not form any definite muscles of the antennae in the embryonic stage. The mesoderm of the antennae seem to give rise to the antennal muscles only either prior to hatching of the larva or after the hatching.

The large hollow ingrowths of the ectoderm arising from the hinder angle of the mandibles (Fig. 99, Plate 19; Fig. 111, 112, Plate 22;

Fig. 129 Plate MND. APD) become associated with the enlarging adjacent mass of the mesodermal cells (Fig. 97, Plate 18; Fig. 99, Plate 19; Fig. 111, 112, Plate 22; MSD). The mesodermal cells can be seen arranging themselves into the form of radiating columns of cells. These radiating columns of cells give rise to the muscles, the great flexor muscles of the mandibles (Fig. 129, Plate 25; MND. MSL).

(ii) *The muscles of the alimentary canal:*

The muscles of the fore-gut are derived from the pre-oral mesoderm which while spreading into the protocephalon surrounds the stomodaeal invagination from all the sides. This mesodermal mass is seen adhering on the outer wall of the stomodaeum throughout the development. It becomes somewhat thinner as the stomodaeal tube increases in length. The sheath of the mesoderm thus surrounding the stomodaeum ultimately gives rise to the musculature of the fore-gut.

The splanchnic mesoderm, which differentiates after the formation of the coelomic sacs from the segmental mesoderm, becomes associated with the developing wall of the mid-gut. With the subsequent development of the mid-gut, when the two mid-gut ribbons grow upwards along with the dorsal expansion of the lateral ectodermal walls of the body and push their way downwards and inwards between the yolk, over the epinural sinus and the nerve cord, the splanchnic layer of the mesoderm is also carried along with it.This layer of mesoderm forms a very thin coating around the mid-gut wall which gives rise to its musculature.

The musculature of the proctodaeum is mainly derived from the mesoderm of the last abdominal segment which surrounds the inpushing proctodaeal invagination. This mesodermal mass during the subsequent development of the proctodaeum spreads along with it in the form of a sheath round it. The mesodermal sheath surrounding the proctodaeum is somewhat thicker than the mesodermal sheath surrounding the stomodaeum. The mesoderm round the proctodaeum differentiates into the muscles of the hind-gut.

Diagrams representing the development of mesoderm in association with the fore-, mid and hind-gut have already been referred to in dealing with the development of the alimentary canal

(iii) *Muscles of the thorax and abdomen:*

The muscles of the thorax and abdomen develop from the somatic layers of mesoderm and the mesodermal mass which is withdrawn while the epinural sinus is formed.

When the body wall spreads upwards over the yolk to meet eventually on the dorsal side, the somatic mesoderm separates out into three masses. One of these is the segmentally arranged mass of cells adjacent to the terga of the body wall dorsal to the spiracular openings. From here the tergal muscles arise. The other masses are in the sternal region, of which one is derived from the mesoderm withdrawn during the formation of the epinural sinus and lies dorso-lateral to the nerve cord, from these the first and second oblique muscles seem to arise. The third mesodermal mass is in the lateral body-wall ventral to the first below the spiracular opening. The muscles of the spiracles and the transverse muscle bands arise from this mesodermal mass (Fig. 85, Plate 16; Fig. 89, Plate 17; Fig. 93, 94, Plate 18; Fig. 114, 115, 116, Plate 22; Fig. 120, Plate 23; Fig. 125, 127, Plate 24; Fig. 128, Plate 25; S. S. MSD; MSD; MSL).

In the prothorax, on the lateral sides strong muscle bands can be seen on either side in a longitudinal section with their origin on the prothoracic wall and their insertion on the head capsule (Fig. 87 Plate 17; MSL). These muscles seem to have arisen from the above mentioned first mesodermal mass of the prothoracic region.

THE NERVOUS SYSTEM

Shortly after the process of gastrulation is completed, the brain and the ventral nerve cord arise from the ectoderm. The nervous system is formed as a result of differentiation of specialised cells of the ectoderm which are called the neuroblasts. The differentiation of the neuroblasts takes place early during the development even before the segmentation of the germ-band is well advanced.

The differentiation of the neuroblasts takes place after 90 hours of incubation (Fig. 38, Plate 8). Certain ectodermal cells on either side of the midventral line become differentiated (Fig. 38, Plate 8; NRB) and can be easily distinguished on account of their large size, with their cytoplasm staining lighter than the adjoining cells. At the same time the neural groove appears in between the neuroblasts of either side (Fig. 38 Plate 8; NR. GR). The neuroblasts enlarge, lose their columnar shape and are withdrawn inside forming an inner layer while the undifferentiated cells of the ectoderm withdraw to the outside, become single-layered with their size smaller and constitute the dermatoblasts (Fig. 38, Plate 8; DBL). The ectoderm at this period presents a pair of thickenings along the sides of the midventral line. The differentiation of the neuroblasts is first initiated in the anterior region and then gradually spreads backwards.

Thus along the entire length of the embryo two continuous cords of neuroblasts arise. The neuroblasts in the beginning are not more than two in a row but in the later stages as many as four of them can be seen (Fig. 40, Plate 9; NRB).

The nerve cells arise from the unequal division of the neuroblasts, the resulting cells are smaller, take a deep stain and form columns of cells above the parent neuroblasts (Fig. 38, Plate 8; Fig. 40, Plate 9; NCL). The origin of the nerve cells in this manner have been described in Korotoneff's (74, 75) account for *Gryllotalpa* and by Wheeler (157, 159) for *Xiphidum.*

During the subsequent development the two lateral cords enlarge and as a result of this bulge out on the surface on either side of the mid-ventral line of the embryo. Due to this bulging of the lateral cords a groove appears in between them constituting the neural groove (Fig. 106, Plate 21; NR. GR).

Above the roof of the neural groove on the inner side along the median line a narrow cord can be seen in addition to the two lateral cords. The cells of the median cord are narrow and columnar. In this region there is no differentiation of the dermatoblasts as described for the lateral cords, but its cells, the neurogenic cells abut on the floor of the neural groove (Fig. 40, Plate 9; M. N. CD).

Although cell division takes place among the neurogenic cells but it is not so pronounced as in the case of the lateral cords where the cell division of the neuroblasts is much more extensive. They are for the most time, during the development, above the neural groove and are of rather large size. Yet they constitute a part of the nerve ganglion between the unfused halves of either side of the ganglion (Fig. 93, Plate 18; Fig. 100 Plate 19; M. N. CD).

The incorporation of the median cord into ganglia has also been recorded by various authors like Hatschek (37), Graber (25 to 31), Heider (44,45), Heymons (54) as well as Tiegs and Murray, (150). Their incorporation into the ganglia was first observed by Graber and Wheeler (156 to 161) was first to show that they become applied only to the hinder wall of the preceding ganglia. Paterson (111, 112, 113) is of the opinion in her observations for *Coryńodes* and *Euroype* that the median cord intera-segmentally gives rise to the transverse commissures which run into the ganglionic fibres developed from the ganglion cells and thus the two ganglia are connected. The observation for *Mylabris* is in agreement with those observed by Paterson. This condition is best seen in a transverse section (Fig. 83, Plate 16; Fig. 93, Plate 18; M.N.CD).

Hatschek and Wheeler are of the opinion that the median cord cells contribute in the formation of the sternal integument. The dermatoblasts from the side of the neural groove seem to grow with the result that the neural groove disappears. It seems most certain that the sternal integument is thus contributed by these dermatoblasts described above and not by the median cord cells as observed by the above mentioned authors.

While these developments are taking place the germ-band has divided into the definitive segments in the head, thorax and the abdominal region. As a result of this segmentation the nerve ganglia are also segmentally arranged. The number of the differentiations of the nerve ganglia is 16 one each from the mandibular to the 10th abdominal segment. In addition to these three more centres of differentiations can be seen which contribute in the formation of the brain. Of these the origin of the third or the tritocerebral is in between the mandibular and the second or the deutocerebral ganglia and is in continuation with the two. It however occupies a postero-lateral position with regard to the stomodaeum. The deutocerebral and the first or the protocerebral ganglia arise pre-orally (Fig. 65, Plate 12; PTC. DEU).

During the subsequent development in the advanced embryos the nerve cords become separated from the ectoderm (Fig. 96 Plate 13; Fig. 93, Plate 18; Fig. 100, Plate 19; V. NR. CD). The ganglia become well consolidated and the two from either side come very close to fuse together giving rise to the segmental ganglion. In the intersegmental regions though the two cords are approximated close to one another they retain their individuality and constitute the paired longitudinal commissures between the succeeding ganglion (Fig. 117, 118 Plate 23; V.NR. CD). In the intra-segmental region due to the extreme consolidation, the transverse commissures become obliterated, yet in transverse sections the indication of the fusion of the ganglionic halves of either side can be easily seen (Fig. 92, Plate 18; Fig. 123, 127, Plate 24; Fig. 128, 130 Plate 25; V.NR.CD).

The sub-oesophageal ganglionic mass is formed by the fusion of the three ganglia of the gnathal segments viz. the mandibular, the maxillary and the labial. These three ganglia after becoming separated from the ectoderm come closer and closer to each other and ultimately fuse giving rise to the consolidated sub-oesophageal ganglion. The formation of the sub-oesophageal ganglion by the fusion of the three ganglionic masses can be seen as late as 194 hours.

In longitudinal sections passing through the anterior end of the embryro, though the three ganglionic masses have fused together yet they can be easily recognised (Fig. 71, Plate 13; Fig. 78, 80, Plate 15; Fig. 82, 83, Plate 16; MND. GN, MX. GN, LB.GN; represent all the above mentioned stages).

All the three thoracic ganglia remain separate throughout and there is no fusion of these three ganglia (Fig. 67, Plate 13; Fig. 78, Plate 15; GN, 1THX.GN). There is no contribution of a few nerve cells from the last (11th) abdominal ganglion as observed by Tiegs and Murray in *Calendra*. The abdominal ganglia of the ninth and tenth segments fuse during the later stages of the development thus the number of the abdominal ganglia which was originally ten becomes reduced to nine (Fig. 84, Plate 16; Fig. 91, Plate 17; V. NR.CD).

THE BRAIN

As already stated the differentiation centres of the components of the brain arise in three different regions. There is no difference in the method and origin of the neuroblasts in these regions from that for the ventral nerve cord already described.

All the three component ganglia become differentiated at the same time when the ventral ganglia are differentiated. The tritocerebral ganglion is the smallest of all the three and is in continuation with the mandibular behind and the deutocerbral ganglion in front. This lies in front of the mandible and occupies a postero-lateral position with regard to the stomodaeum (Fig. 62

Plate 12; TTC). The deutocerebral is farily large and occupies a position at the base of the antennae (Fig. 67, 68, Plate 13; Fig. 74, Plate 14; DUE). The protocerebral is the largest of the three and occupies a great part of the head lobe. (Fig. 67, 68, 70, Plate 13; PTC).

The ganglia of the brain retain their connections with the ectodermal wall for a much longer time and their subsequent separation is brought about very late in the embryonic period. (Fig. 74, 76, 77, Plate 14). The separation is brought about after 194 hours of development and by this time the ventral nerve cord has well separated and even the fusion of the mandibular, maxillary and labial ganglion has just started, the process by which the sub-oesophageal ganglion arises. This can be seen in Fig. 82 plate 16 in a longitudinal section of the embryo through the anterior end in which the three gnathal ganglia have started fusing with each other while the lobes of the brain have just started separating from the ectodermal wall. The tritocerebral ganglion however separates a little early from the ectodermal wall than the proto.or deutocerebral ganglion.

Regarding the origin of sub-oesophageal commissure, Tiegs and Murray are of the opinion in *Calendra*, it is contributed from the tritocerebrum. According to Heymons it is said to be derived from the median cord cells associated with that ganglion. The observations of Heymons are further confirmed by strindberg for *Eutermes* and by Carriere and Bürger (11) for *Chalicodoma*. Paterson has derived it by the ganglion itself in case of *Corynodes*. In the present work I have however failed to draw any conclusion regarding this point.

The circum-oesophageal commissure developes from the tritocerebrum and connects the brain with the sub-oesophageal ganglion. The circum-oesophageal commissure surrounds the stomodaeum. In the longitudinal section passing through the anterior end of the emrbryo this connection can be seen verly clearly (Fig. 82, Plate 16; C.O.COMM).

The head ganglia subsequently become very massive and are eventually separated from the ectoderm. The deutocerebrum merges into the protocerebrum (Fig. 77, Plate 14; Fig. 82 Plate 16; Fig. 97 Plate 18; DUE, PTC). The antennary nerves innervating the antennae arise from the deutocerebrum (Fig. 82 Plate 16; NRV).

The anterior most lobe of the protocerebrum is devoid of any neuroblasts. This portion later forms the optic ganglion. This portion shows a peculiar type of invagination (Fig. 77, Plate 14). Such a invagination has been observed for *Acilius* by Patten (114, 115) and by Wheeler for *Xiphidium*. It has also been observed by Heymons and for *Calendra* by Tiegs and Murray. The ultimate fate of this invagination is not yet known with certainty. Tiegs and Murray have observed this to persist as an almost imperceptible cleft for a much longer time. According to Heymons the invaginated cells seem to degenerate. I have not observed this invagination to persist for a much longer time and the ultimate fate of this could not be detected in the present work. The invagination disappeared shortly after its appearance.

The two ganglia of the brain viz. the proto and duetocerebrum after their separation from the ectoderm are at first widely separated from each other. During the subsequent development the deutocerebral ganglia become incorporated with the protocerebrum yet their individuality can be seen throughout the embryonic development. The tritocerebrum merges completely in the hinder margin of the deutocerebrum. (Fig. 77, Plate 14; Fig. 82, Plate 16; PTC, DUE).

As the consolidation of the head capsule takes place with the subsequent development of its lateral and dorso-lateral walls the ganglia increase further in size and most part of the head cavity is now occupied by the protocerebrum itself. The two protocerebral lobes of either side due to the enormous increase in their size become approximated dorsally. Although they come very near to each other yet there is no connection established between them. The supra-oesophageal commissure is first noticed after 194 hours of incubation. (Fig. 98, 99, Plate 19). In frontal sections passing through the brain and the two protocerebral lobes, the narrow yet well defined supra-oesophageal commissure can be seen connecting the two lobes (Fig. 99 Plate 19; SUP.OES.COMM). A somewhat deep mid-dorsal ectodermal groove can be seen in the same figures as well. According to Paterson, in *Corynodes*, from its cells nerve fibres are developed which establish the connection between the two protocerebral lobes. In *Forficula*, Heymons is also of the same opinion regarding the origin of the supra-oesophageal commissure. This observation has been further confirmed by Eastham for *Pieris*.

In *Mylabris* however there seems to be no definite proof of cells arising from the ectodermal groove but on the contrary the supra-oesophageal commissure is derived from the ganglia itself. This is in full agreement with the observations of Villanes (152) for *Mantis*, Wheeler for *Xiphidium* and Strindberg for *Eutermes*. In *Calendra* a similar median depression has been observed by Tiegs and Murray but the authors are of the opinion that the wall of the depression does not contribute in the formation of the supra-oesophageal commissure.

During the subsequent development the two ganglia from either side come more closer and eventually fuse with each other in the dorso-median line just above the stomodaeum. The supra-oesophageal commissure becomes incorporated in them and is no more to be seen (Fig. 113, Plate 22; Fig. 121, Plate 23; BR).

STOMATOGASTRIC NERVOUS SYSTEM :

The anterior wall of the stomodaeum shows thickening at three places (Fig. 71, Plate 13). From the middle of these thickenings the frontal ganglion arises. It is constricted off from the stomodaeal wall and can be seen closely applied to it in the beginning (Fig. 80, Plate 15; FR.GN). It then comes to lie at some distance from the stomodaeal wall and the mesoderm surrounding the stomodaeum separates the two (Fig. 83 Plate 16; Fig. 99, Plate 19; Fig. 121, Plate 23; FR.GN). The origin of the recurrent nerve, the occipital ganglion and the paired pharyngeal ganglia could not be studied.

Heider (45) was first to observe that the frontal ganglion and the recurrent nerve originate as an evagination of the dorsal wall of the stomodaeum. Heymons (55) found in Orthoptera and Dermaptera that the Stomatogastric system is derived from three medially lying evaginations of the stomodaeal wall. In *Locusta migratoria*, Roonwal (127) agrees with this view, the only difference being that in all the forms the ventricular ganglion is unpaired, in *Locusta*, as in all Saltatoria, it is paired.

Very few references regarding the development of this system in Coleoptera are to be found. Heider (45) states the origin of frontal ganglion with its recurrent nerve from the invagination in the stomodaeal wall but Wheeler (161) refers only to the frontal ganglion. In *Calendra oryzae*, Tiegs and Murray (150) have noted the origin of the system as three invaginations of the stomodeal wall, whereas Wray (164) notes only one in *C. callosa*.

SYNOPTIC TABLE OF DEVELOPMENT AT DIFFERENT HOURS OF INCUBATION

Summary of development at different hours of incubation, from oviposition upto 72 hours, already has been given on pp. 452-453 in my paper published in Agra University Journal of Research (Science), Vol. III, part 2; July 1954. The following is the summary of development in continuation after 72 hours of incubation.

Incubation period	*State of development.*
75 hours	The gastrular groove at the posterior end deepens further and a faint groove appears at the anterior end of the germ-band where also the cells proliferate. The primary dorsal organ still persists.
78 hours	The inner layer spreads uniformly along the entire length of the germ-band. The germ-band is sunk deeper in the posterior end. The embryonal envelopes make their appearance in the posterior region .
81 hours	The embryonic envelopes are complete. The anterior and the posterior ends of the germ-band have gone still deeper into the yolk. The germ-band shifts from postero-ventral region to mid-ventral region of the egg. The primary dorsal organ disappears.
85 hours	The anterior end is drawn out while the posterior end is still inside the yolk. The germ-band divides into an anterior broader and a posterior narrow portion.

90 hours	The posterior narrow portion divides into an anterior broader and a posterior narrow portion. The anterior portion shows further faint lines of segmentation giving rise to gnathal and thoracic segments.
94 hours	First two abdominal segments appear. The germ-band is fully withdrawn out of the yolk and grows in length. The blastokinetic movements are over. The neuroblasts are differentiated.
100 hours	The remaining portion of the abdomen also becomes segmented. The antennae appear. The stomodaeal invagination alsoappears.
106 hours	The paired appendages grow as out-pushing of the ectodermal wall. The mandibles are the largest. The dermatoblasts are formed. The neural groove deepens and the median nerve cord is differentiated. The nerve cells arise. The labrum makes its appearance. The anterior endoderm rudiments are differentiated.
112 hours	The proctodaeal invagination arises. The appendages become prominent and the mesoderm is drawn into their cavities. The stomodaeum deepens further. The anterior endoderm rudiment grows backwards reaching upto the first maxillary segment in the form of lateral ribbons.
118 hours	The lateral ribbons reach nearly upto the second maxillary segment. The proctodaeum curves towards the anterior egg pole and the posterior endoderm rudiment appear at its blind end.
124 hours	The antennae occupy a pre-oral position. The germ-band in the cephalic region becomes broader and curves upwards at the sides. The posterior endoderm rudiment grows forwards in the form of two ribbons.
130 hours	The mesoderm spreads in the head region. The first and second maxillae show faint line of division.
140 hours	The ceolomic sacs appear from the labial to the last abdominal segment. In the cephalic region small paired antennary coelomic sacs appear. The nerve ganglia as well as the median nerve cord are well separated from the ectoderm while the brain element is not yet separated. The mesoderm in the gnathal and thoracic appendages becomes loose.
150 hours	The coleomic sacs enlarge and the splanchnic and somatic layers of mesoderm are formed. The mid-gut epithelium starts spreading downwards. The brain components are

separated from the ectoderm. In the head region a well defined haemocoelic cavity with blood cells develops. The epineural sinus is formed over the ventral nerve cord. The sub-oesophageal body is differentiated. The appendages are well developed. The maxillary and the labial appendage become constricted into a broader basal and a narrow distal part. The stomatogastric system is differentiated.

160 hours The brain enlarges. The deutocerebrum fuses with the protocerebrum, the tritocerebrum moves forwards. The antennae elongate further. The ectoderm in the head region curves upwards and the cephalic capsule at this stage is oepn only on its dorsal side.

172 hours The proctodaeal opening to the exterior becomes constricted and at its blind end the rudiments of the malpighian tubules also appear. The frontal ganglion is separated off. The fat bodies are differentiated the coelomic sacs enlarge further. The sub-oesophageal body comes to lie in close contact with the mid-gut epithelium. The legs are well developed with the mesoderm penetrating in their cavities. The spiracles are also well developed. The coelomic cavities are partially filled with the fat bodies.

180 hours The mandibular, maxillary and the labial ganglia come closer to each other. The longitudinal commissures in between them become very much reduced. The sub-oesophageal body is no more to be seen. In the inter-segmental regions the coelomic sacs are now separated by very thin septa. The mid-gut epithelial ribbons fuse. The tentorial invaginations are formed. The optic ganglion and the optic plate are differentiated.

194 hours The wall of the blind end of the stomodaeum becomes very thin. The opening to the exterior becomes constricted. The haemocoele extends from the head upto the posterior most region of the abdomen. The fat bodies increase further. The mesoderm surrounding the stomodaeum and the proctodaeum becomes arranged in a more or less uniform layer. The coelomic sacs open on the inner side and a direct communication is thus established with the epineural sinus. The ganglia come closer to one another and the median nerve cord becomes incorporated in them. The circum-oesophageal commissure is established between the deutoecerebrum and the mandibular ganglion. The malpighian tubules grow further in length. The mandibular, maxillary and the labial

ganglia come still closer to each other. The optic plate invaginates forming a cup-like structure. The supra oesophageal commissure is formed. The mandibular apodeme and the tentorium are well developed. The cardioblasts are differentiated.

200 hours The eye is well developed. Muscles in the thoracic and head region are developed. The malpighian tubules are six in number three on either side reaching nearly upto the posterior end of the abdomen along the sides of the proctodaeum. The mesoderm arranges in the form of thin layer around each tubule. The spiracular invaginations deepen further. The mid-gut epithelium is completed on the ventral side. The lateral body wall further grows upwards.

208 hours The antennary coelomic sacs fuse to form the dorsal aorta. The brain now occupies a major portion of the head cavity.

214 hours The brain consolidates further and the supra-oesophageal commissure is obliterated and no more to be seen. The dorsal tentorial arms join with the main body. The mandibular apodeme develops further. The stomodaeum further increases in length and curves towards the posterior egg pole.

224 hours The mesoderm surrounding the mandibular apodeme arranges into radiating branches to give rise to the strong fan-shaped muscles of the mandibles.

232 hours The serosa is thrown upwards forming the secondary dorsal organ. The amnion forms a thin membranous connection between the body wall and the secondary dorsal organ.

236 hours The secondary dorsal organ invaginates and forms an irregular groove in it. In the posterior region the lips of the groove unite with each other enclosing a narrow lumen. Two main tracheal branches are given off from the spiracular invagination—one is horizantal and short, the other is longer and goes towards the dorsal side along the body wall which grows further upwards.

244 hours The brain is further consolidated. The inner lining of the stomodaeum shows a few folds. The dorsal aorta comes to lie close to the stomodaeum which further elongates. The sub-oesophageal ganglion consolidates further and no trace of its component ganglia can be seen.

252 hours The radiating muscles of the mandible develop further. The maxillae and the labium acquire their proper position and their segmentation is complete. The mandibles curve inwards.

264 hours The definite dorsal closure takes place. The secondary dorsal organ is pushed into the yolk where it disintigrates. The stomodaeum at its hinder-most end dialates forming the proventriculus, its portion leading inside from the mouth is very narrow forming the pharynx. The portion between the proventriculus and the pharynx forms the ceosophagus. The mid-gut wall is complete on the dorsal side. Communication between the fore-and mid-gut is established and the opening is guarded by oesophageal valves. The inner lining of the stomodaeum becomes much folded. The muscles are well developed. The tracheae ramify further. The heart, the pericardial cells and the alary muscles are well developed. The haemocoelic cavity is now continuous. The legs are well developed and their segmentation completed. The hind-legs extend even beyond the hinder extremity of the embryo. The proctodaeum becomes coiled and the connection between the hind-and mid-gut opens. The opening being guarded by the procodaeal valves. The inner lining of the proctodaeum also becomes folded. The yolk is completely surrounded by the mid-gut wall. The muscles are well developed. The mandibles are sharp and pointed at their distal ends. The eyes appear as dark brown spots.

EXPLANATIONS OF ABBREVIATIONS USED.

ABD., abdomen; A.END.R., anterior endoderm rudiment; A.L. MSL. alary muscle; AMN, amnion, AMN.C., amniotic cavity; AMN.F. amniotic fold; ANT, antennae; BL. CL., blood cells. BR.C.O. COMM., circum oesophageal commissure; COES. coelomic sacs; CRD., cardioblast. DT. NT.A., Dorsal tentorial arm; ECT. etcoderm; EP.SN., epineural spinus; FB., fat body; FRL. GN., frontal ganglion; GB., germband, GN, ganglion; GST.GR, gastrular groove; HMC, haemo-coele; HBD.L., head lobe; HT. heart; IN.LY. inner layer; LB. labium; LB. GN. labial ganglion LBR. labrum; LG. leg ; LN. lens; MND. mandible; MND.GN. mandibular ganglion; MT., malpighain tubule; MTR., mapghian tubule rudiment; MXI. first maxilla; MX2. second maxilla; MX.GN. maxillary ganglion; MSD. mesoderm; MSL. muscles; NCL. nerve cells; NRB. neuroblasts; N.R.G.R. neural groove; NRP. neuropile; OES. oesophagus; OES oesophageal valve; OP.L., optic lobe; OP.GN., optic ganglion; PCT., proctodeum; PCT., proctodaeal valve; PTC., protocerebrum; PTC. L., protocerebral lobe; PR.O.MG.CL., pre-oral mid-gut cells; PER. CL. pericardial cells; RT.LY., retinal layer; S.D.O., secondary dorsal organ; SBO. B. sub-oesophageal body; SBO. GN., suboesophageal ganglion; SM.MSD., somatic mesoderm; SPL. MSD., splanchnic mesoderm; SP., spiracles; S.S.MSD., subsomatic mesoderm; ST., stomodaeum; SUP. OES. COMM. supraoesophageal commissure; SER. serosa; TENT. tentorium; THX, thorax; TR., trachea; TTC; tirto-cerebrum; NR. CD., ventral nerve cord; YK. Yolk; YKC. yolk cells.

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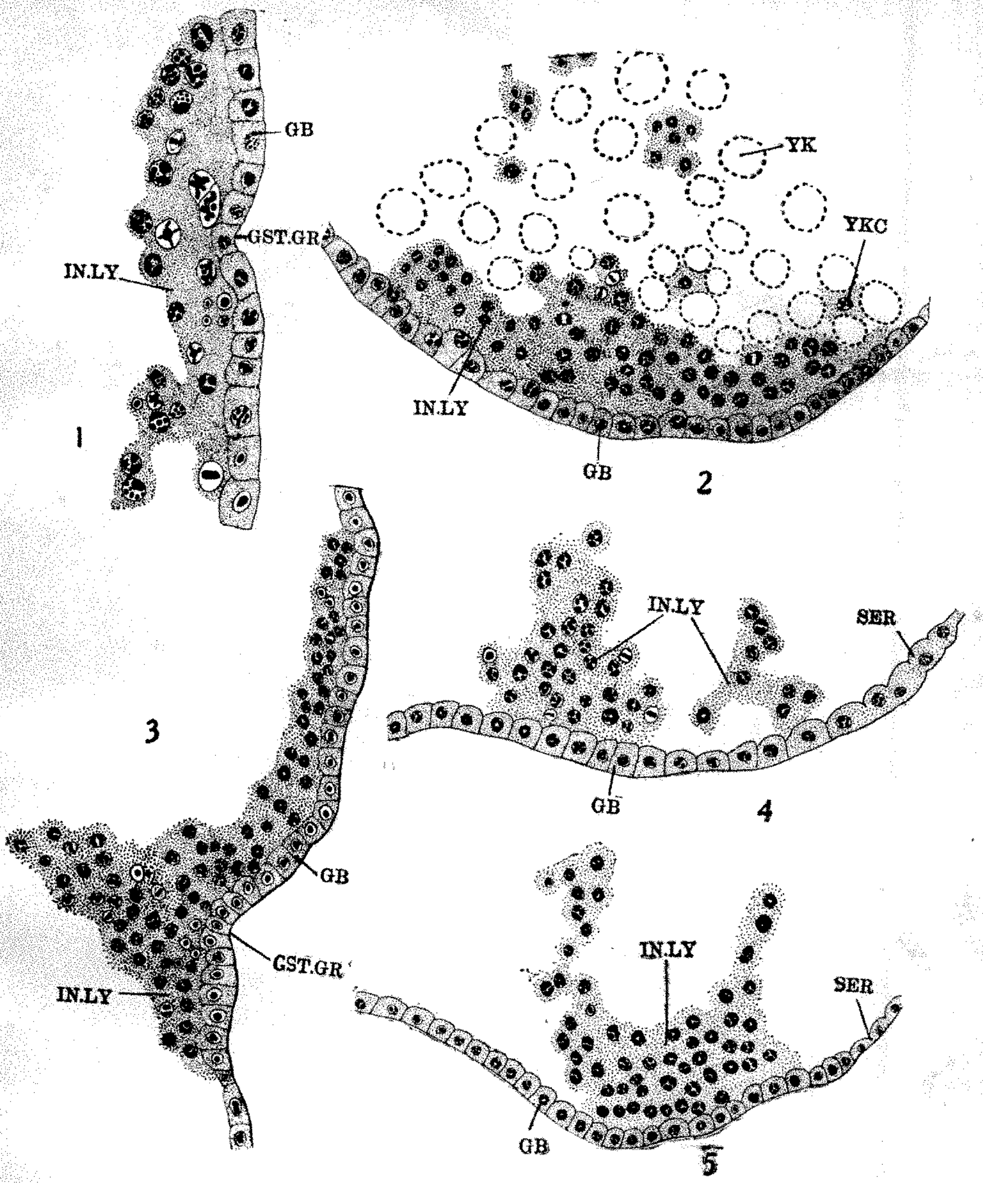
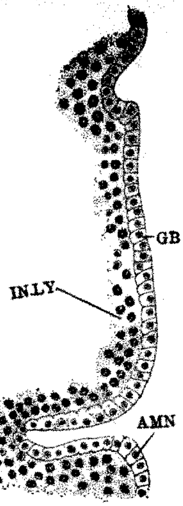


PLATE. 1. Fig. 1. L. S. through the anterior region (46 × 12).
Fig. 2. T. S. anterior end 46 × 8).
Fig. 3. L. S. posterior region (46 × 8)
Fig. 4. T. S. middle region (46 × 8)
Fig. 5. T. S. posterior region (46 × 8).
All the figures represent 75 hours stage.



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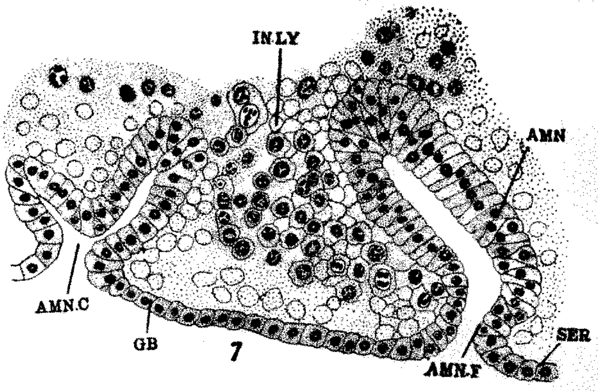

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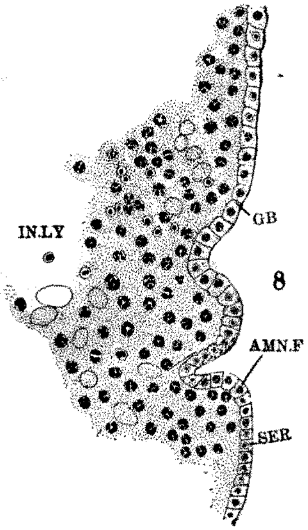

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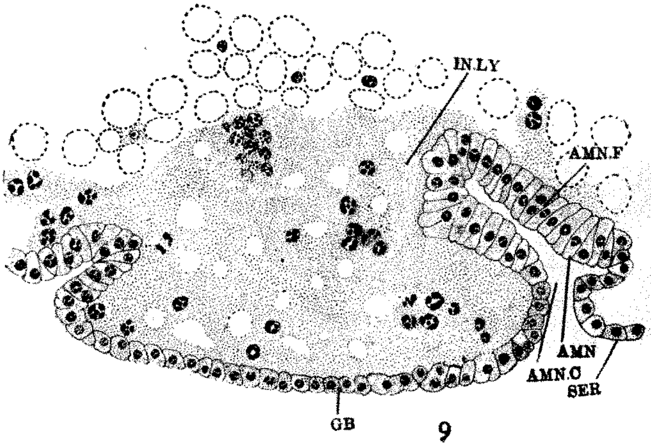

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PLATE 2. Fig. 6. L. S. germband entire (20 × 8).
Fig. 7. T. S. posterior region (46 × 12).
Fig. 8. L. S. posterior region slightly lateral to the mid-ventral line (46 × 8).
Fig. 9. T. S. middle region (46 × 12).
All the figures represent 78 hours stage.

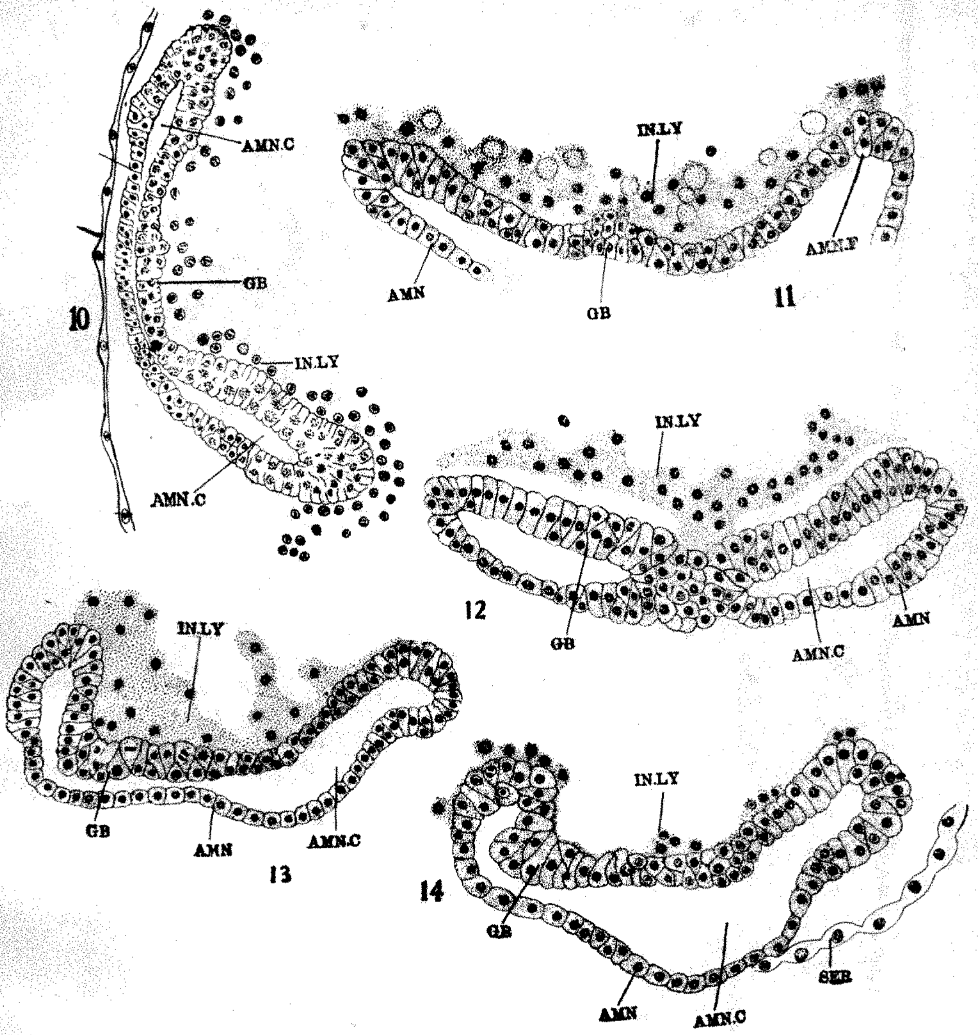


PLATE 3. Fig. 10. L. S. entire germband (20 × 8).
Fig. 11 T. S. anterior region region (46 × 80).
Fig. 12. T. S. middle region (46 x8)
Fig. 13. T. S. slightly behind the middle region.
Fig. 14. T. S. hinder-most region (46 × 8).
All the figures represent 81 hour stage.

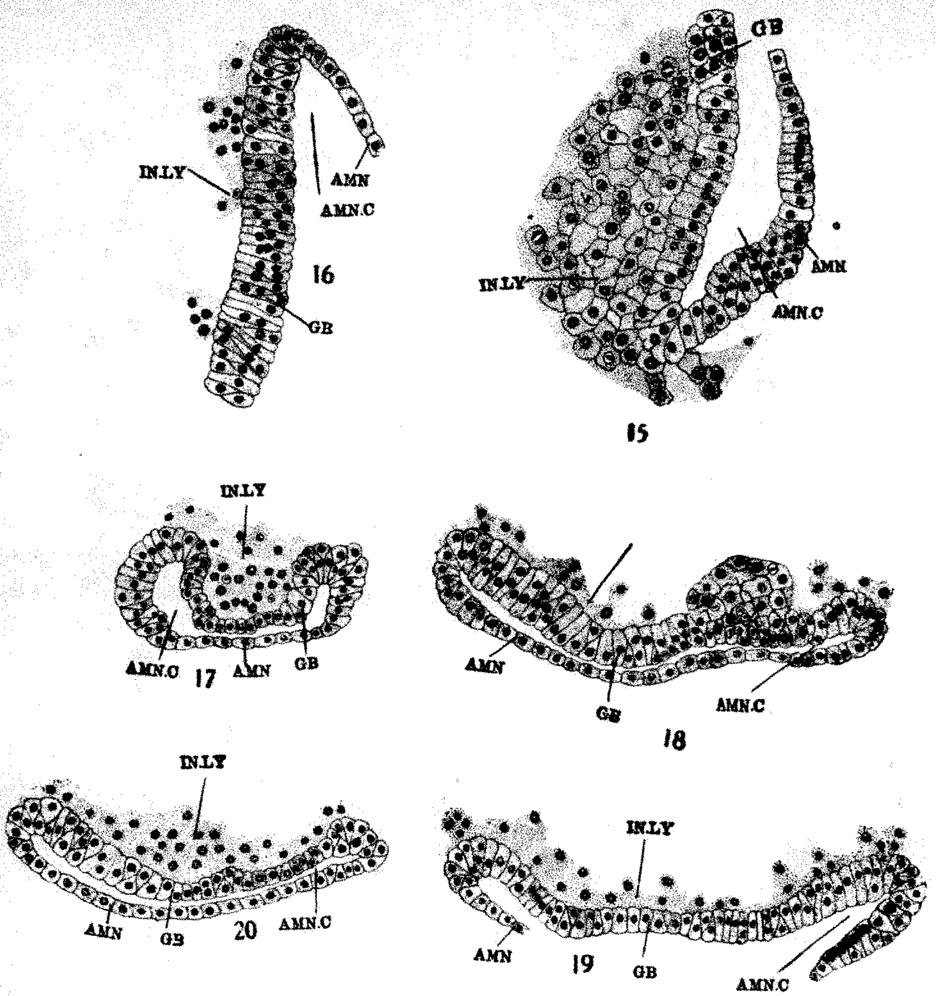
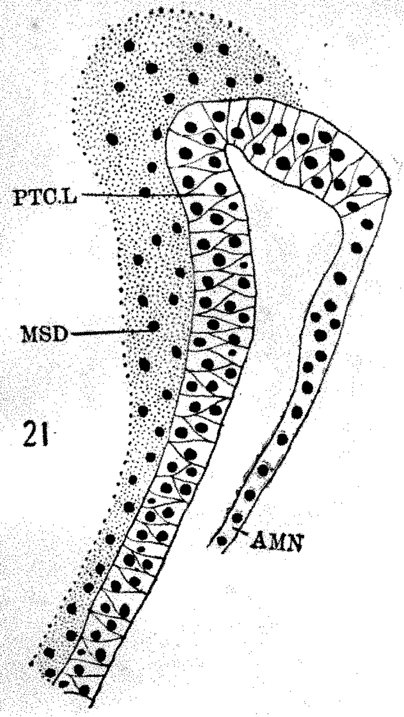


PLATE 4. Fig. 15. L. S. posterior end (46 x 8).
Fig. 16. L. S. anterior end (46 x 8).
Fig. 17. T. S. posterior region (48 x 8).
Fig. 18. T. S. anterior region (46 x 8).
Fig. 19. T. S. anterior region (46 x 8).
Fig. 20. T. S. middle region (46 x 8).
All the figures represent 85 hour stage.



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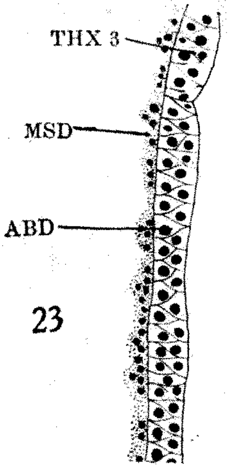

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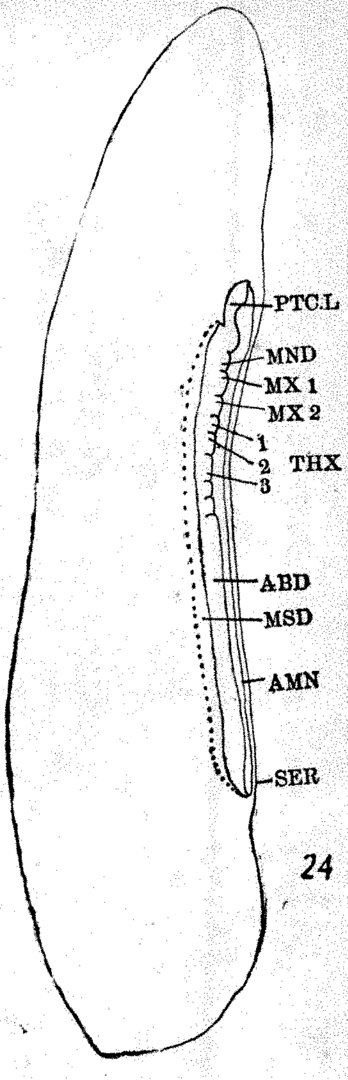

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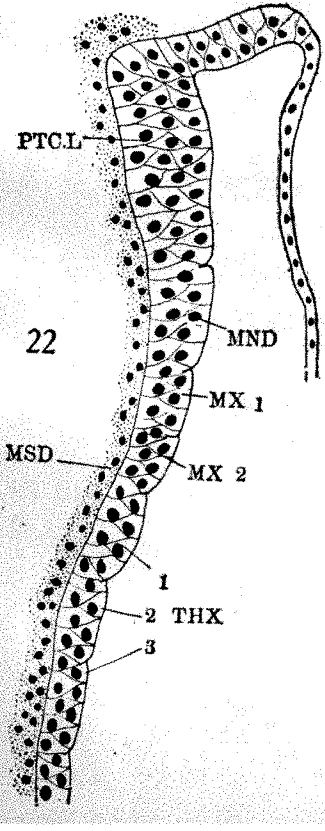

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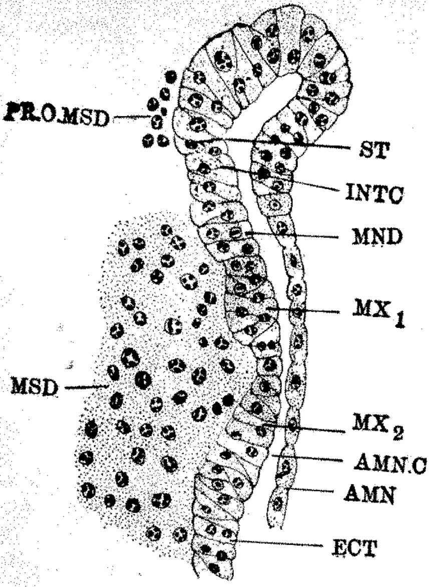
PLATE 5.

Fig. 21. L. S. anterior end (46 × 8).
Fig. 22. L. S. anterior end (46 × 8).
Fig. 23. L. S. thoracic and abdominal region (46 × 8).
Fig. 24. L. S. entire egg (20 × 8).

Figures 21-23 represent 90 hour stage, figures 24 represents 94 hour stage.



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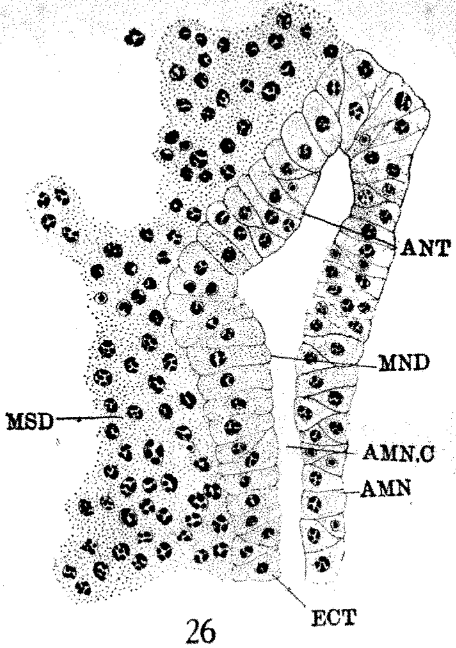

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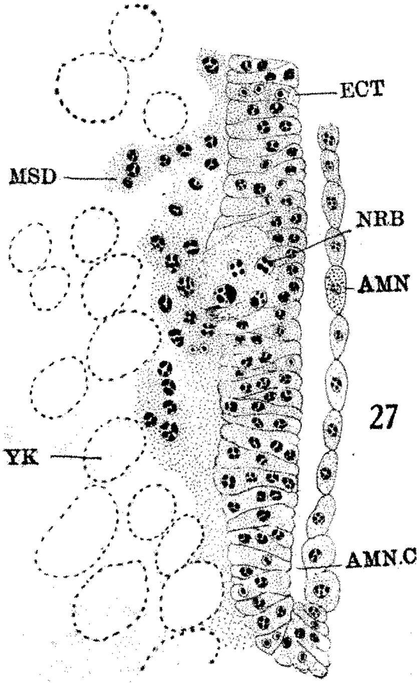

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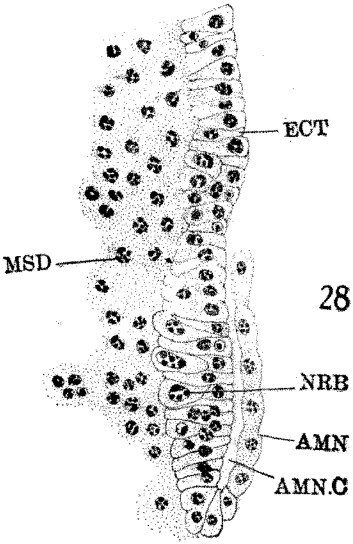
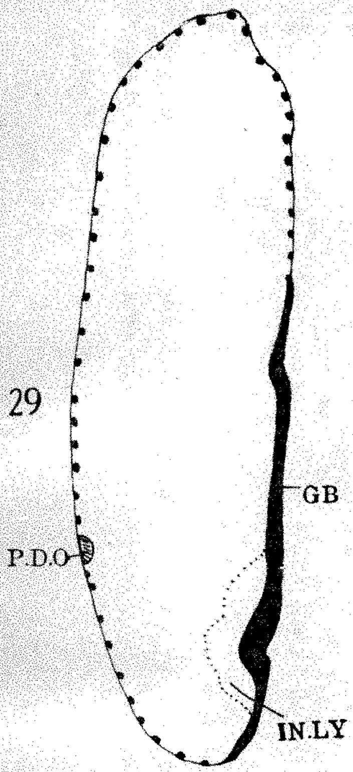


28

Plate 6. Fig. 25. L. S. anterior end mid-ventral line (46 × 12).
Fig. 26. L. S. anterior end (46 × 12).
Fig. 27. L. S. posterior end (46 × 12).
Fig. 28. L. S. posterior end (46 × 12).
All the figures represent 100 hour stage.



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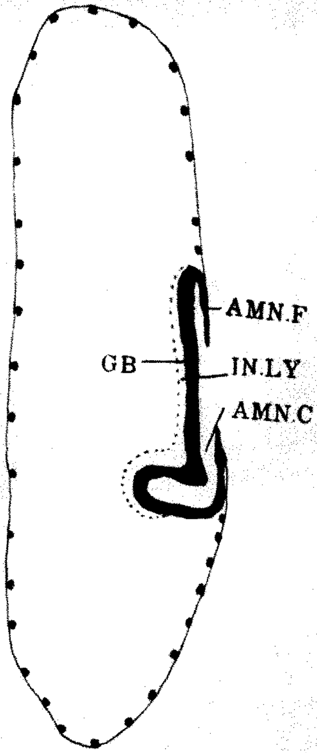

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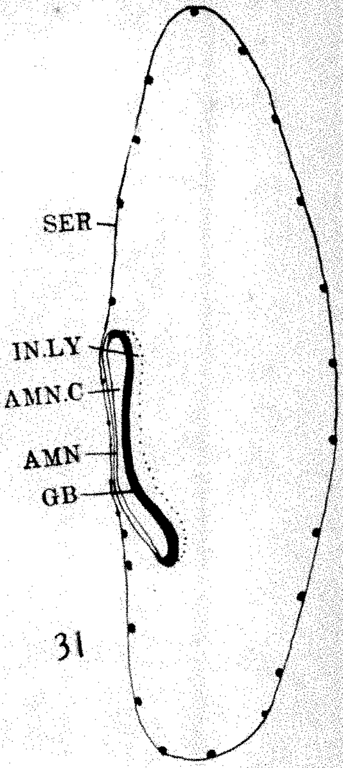

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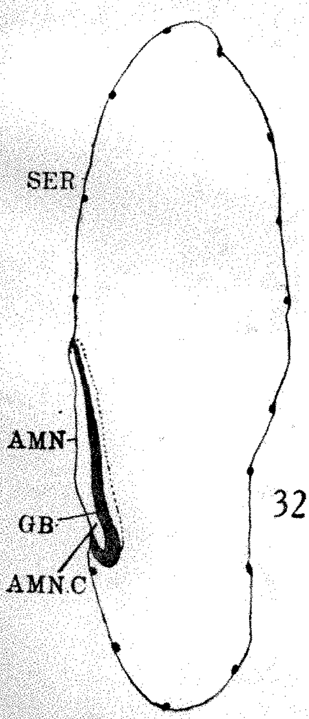

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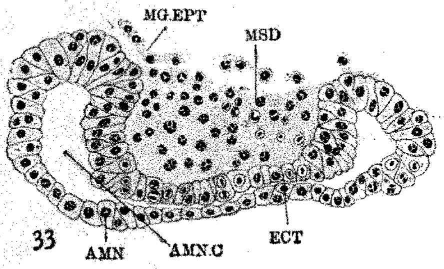
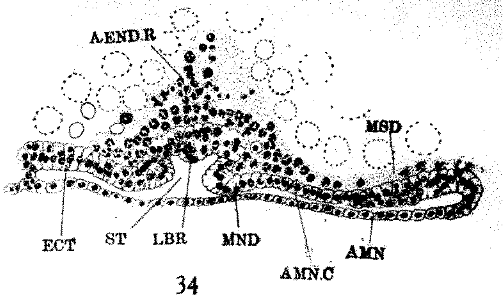
PLATE 7.

Fig. 29. L. S. entire egg 78 hours (20 × 5).
Fig. 30. L. S. entire egg 85 hours (20 × 5).
Fig. 31. L. S. entire egg 90 hours (20 × 5).
Fig. 32. L. S. entire egg 94 hours (20 × 5).





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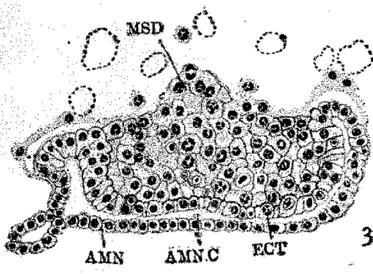

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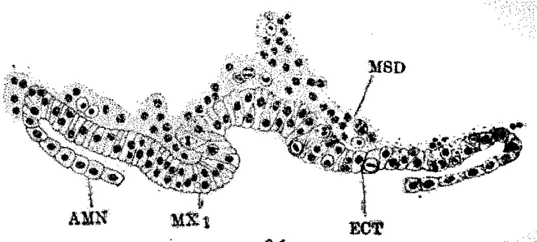

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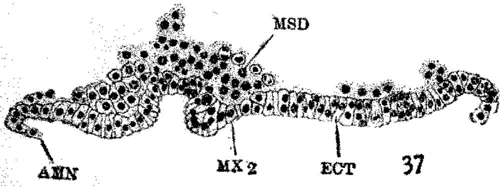

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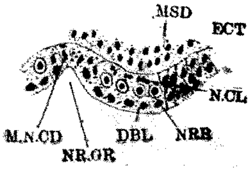
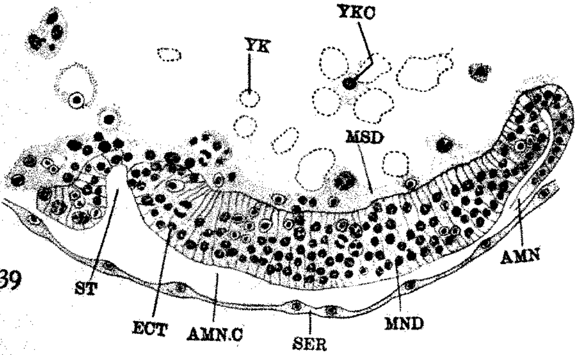


Plate 8. Fig. 33. T. S. posterior end (46 × 8).
Fig. 34. T. S. stomodaeum (46 × 8).
Fig. 35. T. S. middle region (46 × 8).
Fig. 36. T. S. first maxillary segment (46 × 8).
Fig. 37. T. S. second maxillary segment (46 × 8).
Fig. 38. T. S. showing the differentiation of neuroblasts (100 × 8, oil immersion)
All figures represent 106 hour stage.



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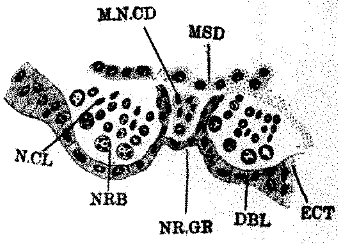

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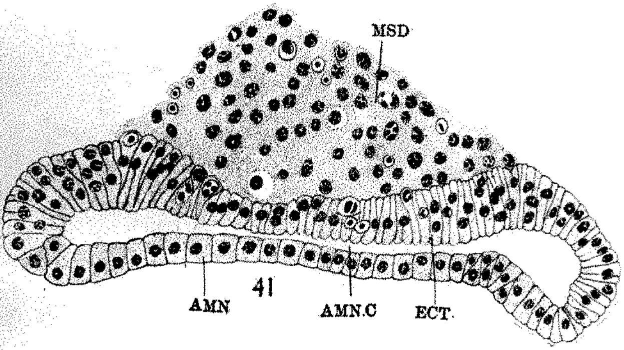

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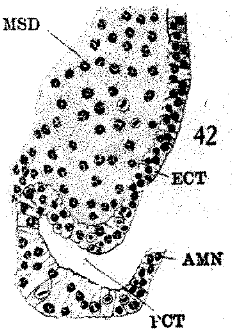

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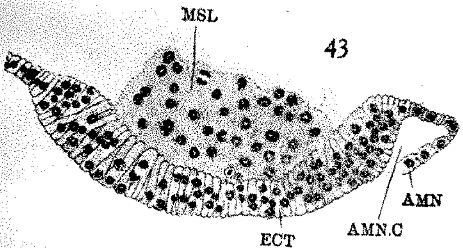

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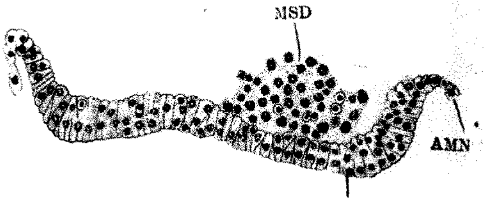

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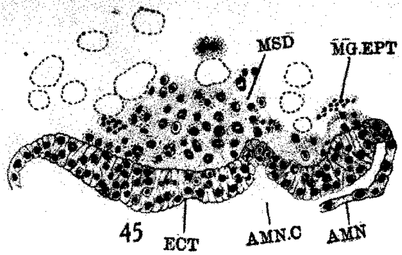
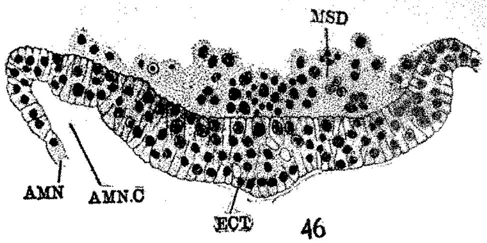
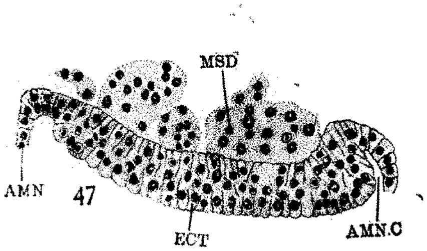
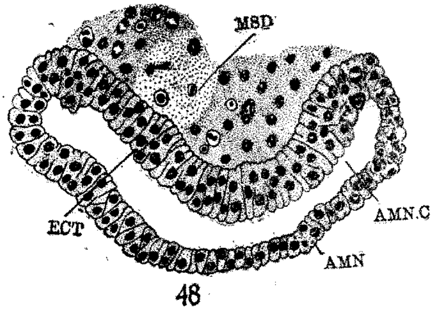
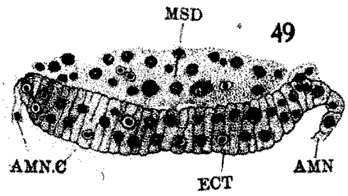
PLATE 9. Fig. 39. T. S. mandibular segment (46 × 12).
Fig. 40. T. S. nerve cord (100 × 8, oil immersion).
Fig. 41. T. S. posterior end (46 × 12).
Fig. 42. L. S. proctodeum (46 × 12).
Fig. 43. T. S. gnathal appendage (46 × 8).
Fig. 44. T. S. thoracic region (46 × 8).
All the figures except figure 42 represent 112 hour stage, figure 42 represents 124 hour stage.

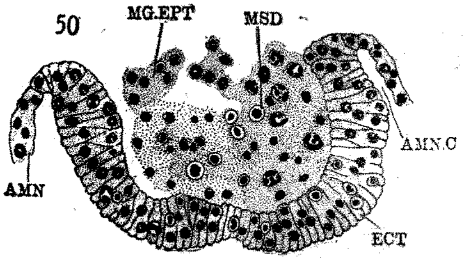












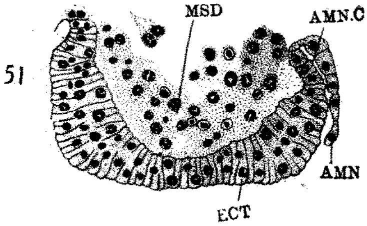
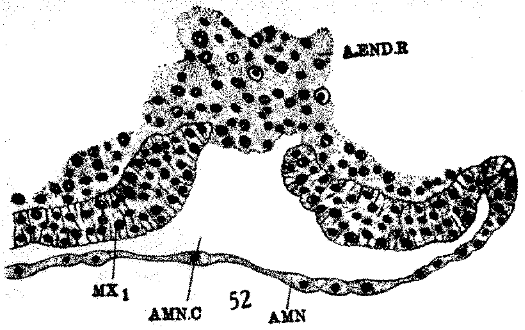


Plate 10. Fig. 45. T. S. maxillary segment (46 x 8).
Fig. 46. T. S. anterior end (46 x 12).
Fig. 47. T. S. thoracic region (46 x 8).
Fig. 48. T. S. slightly in front of the hinder-most end of the abdomen (46 x 8).
Fig. 49. T. S. middle region of the abdomen (46 x 8).
Fig. 50. T. S. hinder-most abdominal end (46 x 8).
Fig. 51. T. S. slightly behind the middle region of the abdomen (46 x 8).
All the diagrams represent 118 hour stage.



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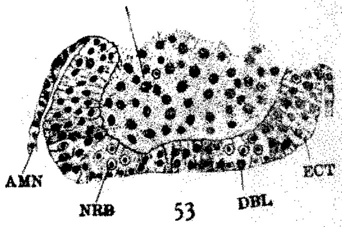

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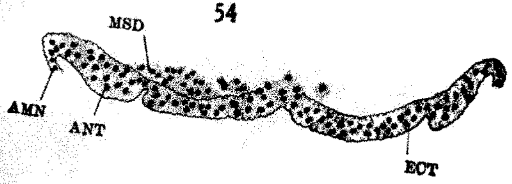

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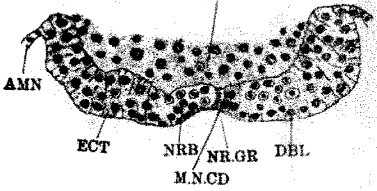

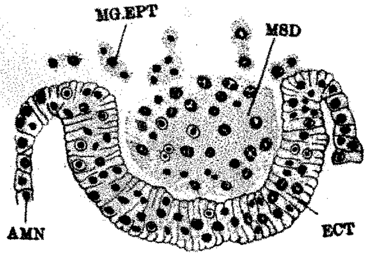

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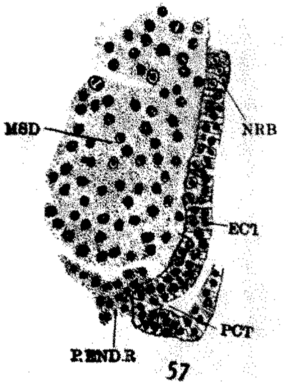

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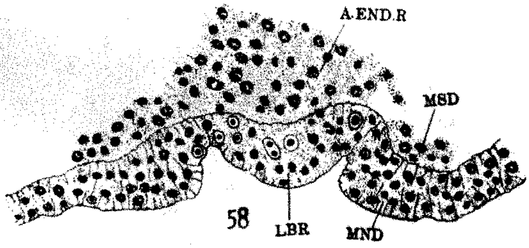

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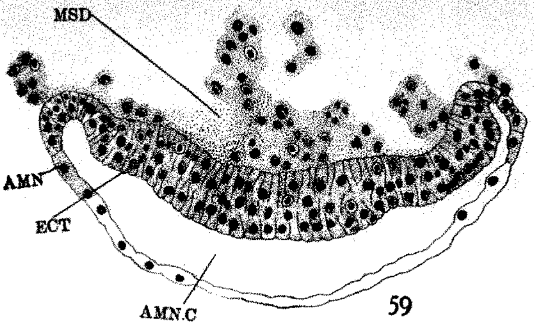
PLATE 11. Fig. 52. T. S. maxillary segment (46 x 12).
Fig. 53. T. S. middle region of the abdomen (46 x 12).
Fig. 54. T. S. head lobe (46 x 8).
Fig. 55. T. S. thoracic region (46 x 8).
Fig. 56. T. S. posterior abdominal end (46 x 8).
Fig. 57. L. S. posterior end, proctodaeum (46 x 12).
Fig. 58. T. S. labrum and mandibles (46 x 12).
All figures represent 124 hour stage.



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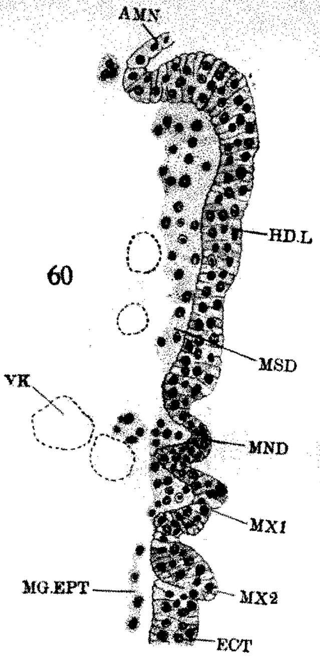

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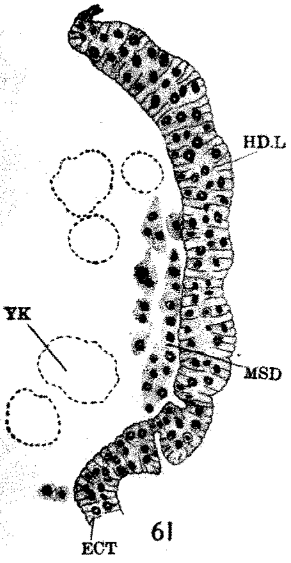

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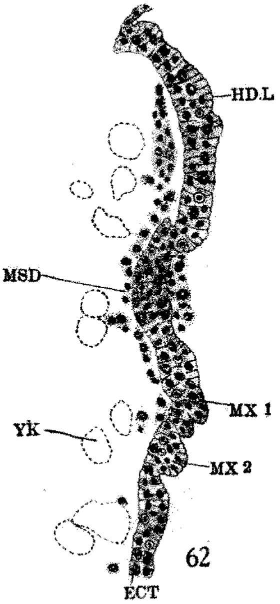

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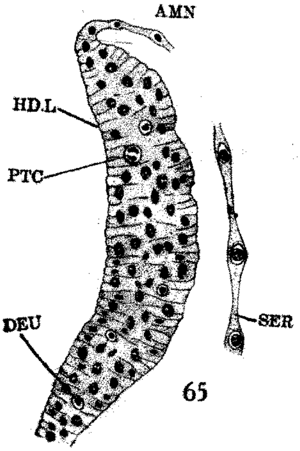

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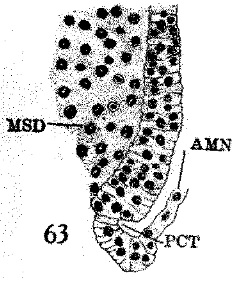

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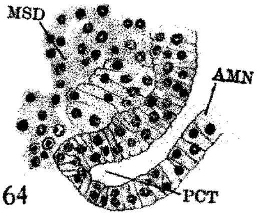

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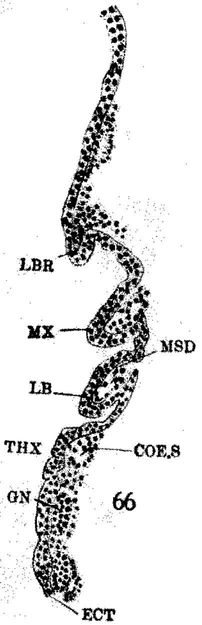
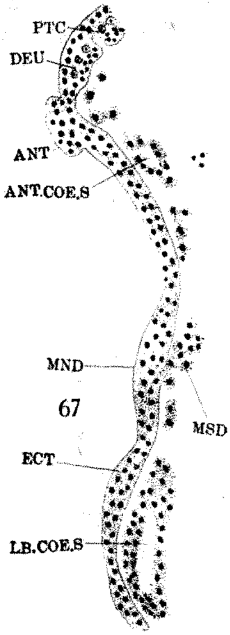
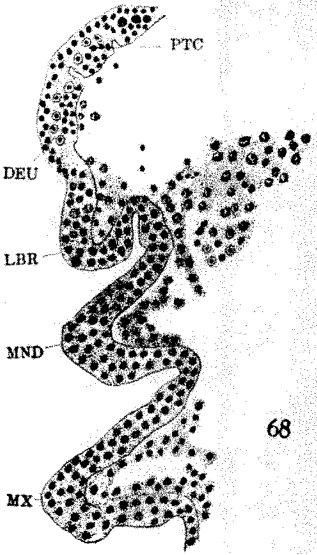
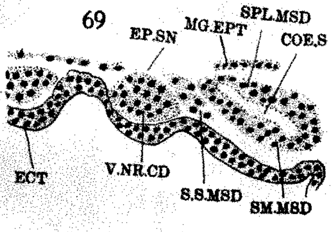
Plate 12. Fig. 59. T. S. through the anterior-most region of the head (46 × 12).
Fig. 60. L. S. anterior end of the embryo (46 × 12).
Fig. 61. L. S. head lobe only (46 × 12).
Fig. 62. L. S. anterior end (46 × 12).
Fig. 63. L. S. posterior end through the proctodaeum (46 × 8).
Fig. 64. L. S. posterior end, proctodaeum (46 × 8).
Fig. 65. L. S. head lobe (46 × 12).

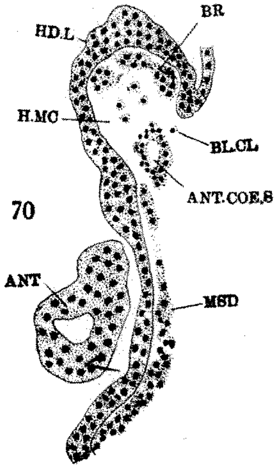
Figures 59-62 and 65 represent 130 hour stage. Figure 63 and 64 represent 112 hour stage.











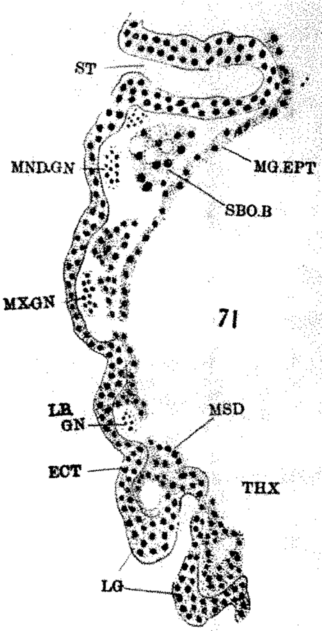
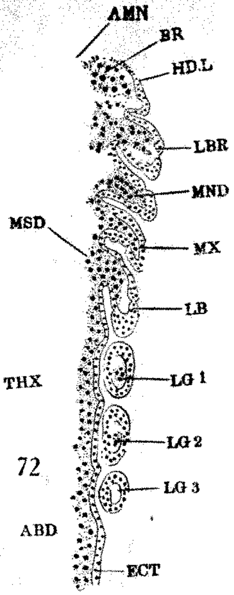
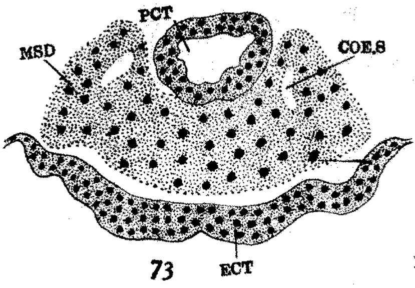
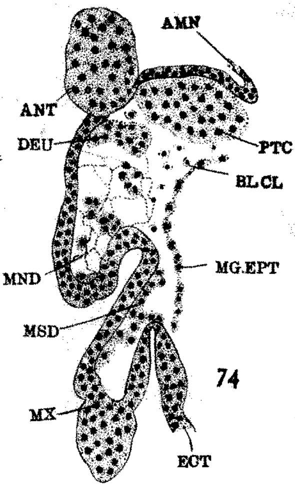
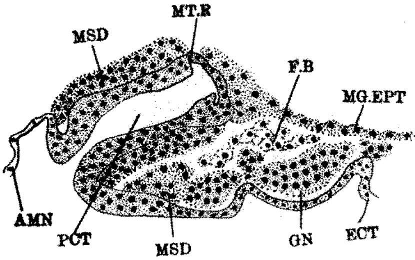


Plate 13. Fig. 66. L. S. anterior end through the gnathal and the thoracic segments (46 × 8).
Fig. 67. L. S. head and gnathal segments (10 × 12).
Fig. 68. L. S. head and gnathal segments (46 × 12).
Fig. 69. T. S. abdominal region (46 × 12).
Fig. 70. L. S. head region with the antennary coelomic sac and the brain components (46 × 8).
Fig. 71. L. S. stomodaeum, gnathal and first abdominal segment (46 × 8).
Figures 66-69 represent 140 hour stage.
Figures 70 and 71 represent 150 hour stage.









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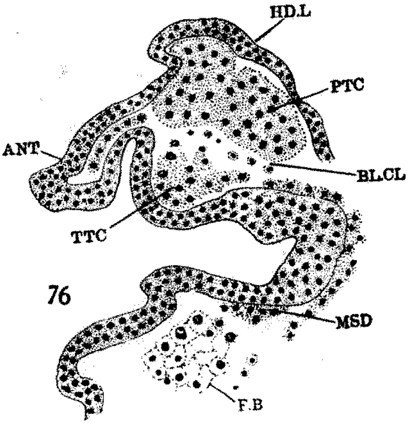


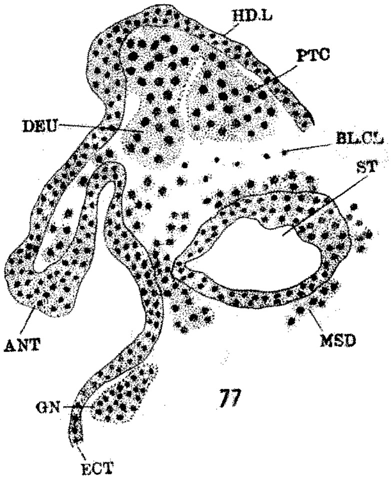
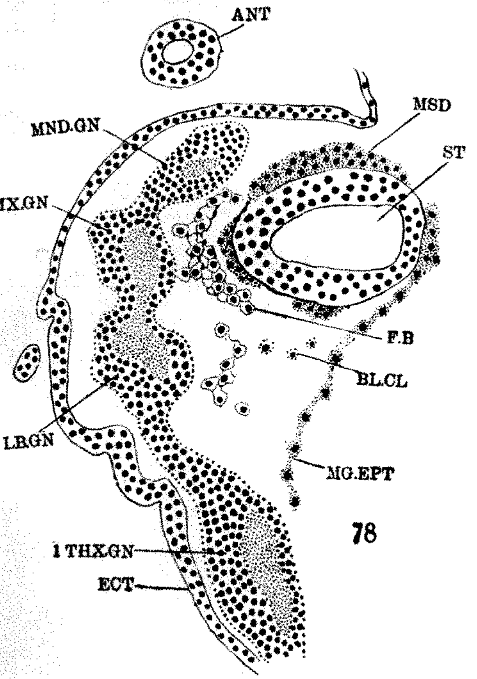


PLATE 14. Fig. 72. L. S. through head, thorax and first abdominal segment (10 × 8).
Fig. 73. T. S. through the proctodaeum (46 × 8).
Fig. 74. L. S. through the head region (46 × 8).
Fig. 75. L. S. through the posterior end showing the proctodaeum (46 × 8).
Fig. 76. L. S. anterior end through the stomodaeum and the head (46 × 8).
Fig. 77. L. S. anterior end through the stomodaeum and the head (46 × 8).
Figures 72, 73 and 75 represent 172 hour, figures 76 and 77 represent 160 hour, and figure 74 represents 150 hour stage.



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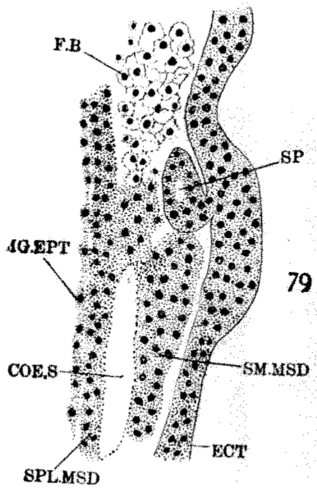

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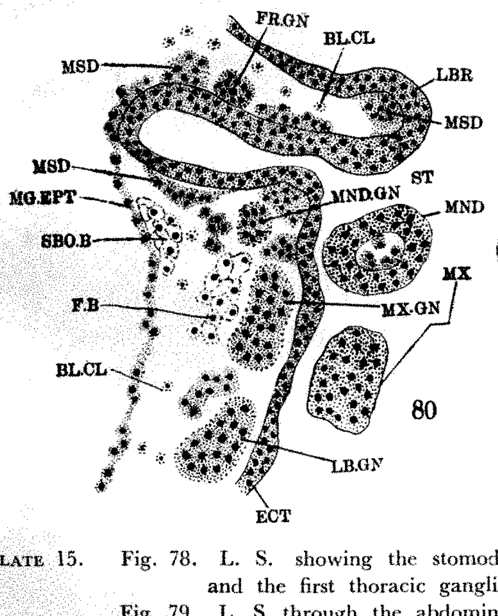

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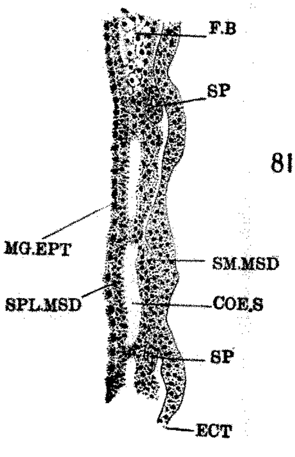

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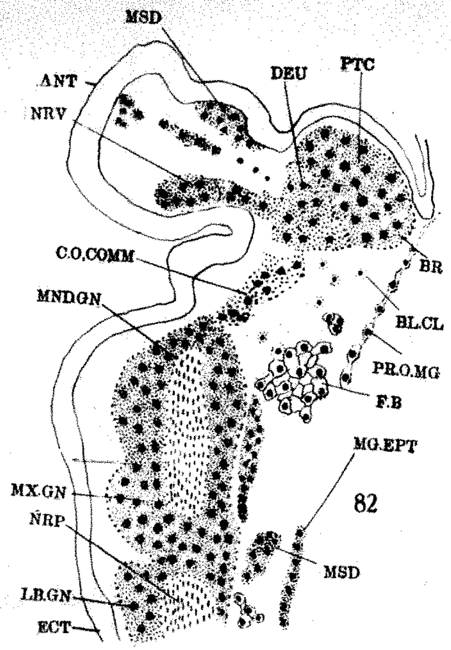
PLATE 15. Fig. 78. L. S. showing the stomodaeum, the mandibular, maxillary, labial and the first thoracic ganglion (46 × 8).

Fig. 79. L. S. through the abdominal region (46 × 12).

Fig. 80. L. S. anterior end passing through the stomodaeum. (46 × 12).

Fig. 81. L. S. through the abdominal region (46 × 8). Figure 78 represents 180 hour and figures 79-81 represent 172 hours stages.



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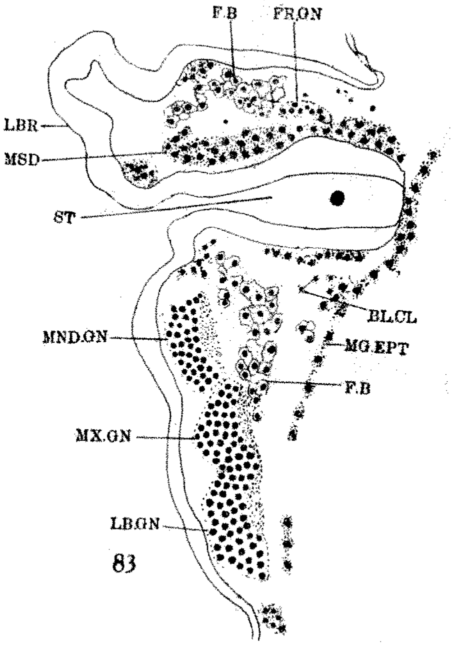

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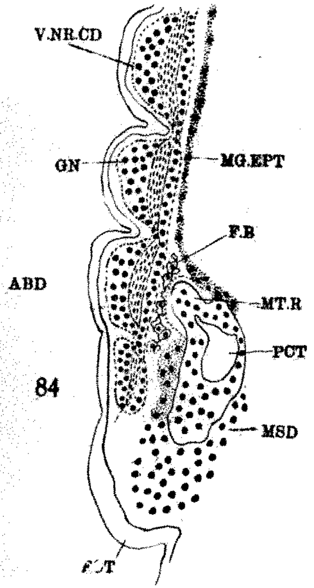

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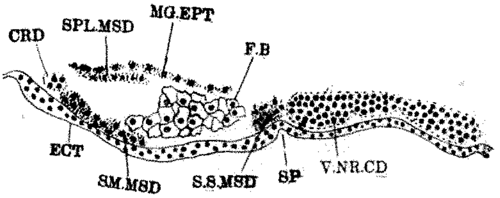

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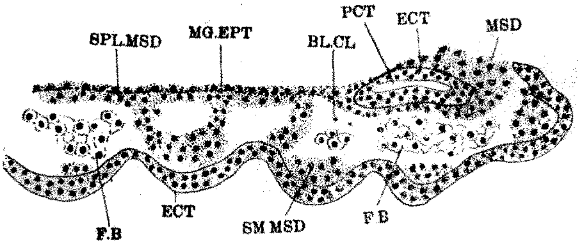

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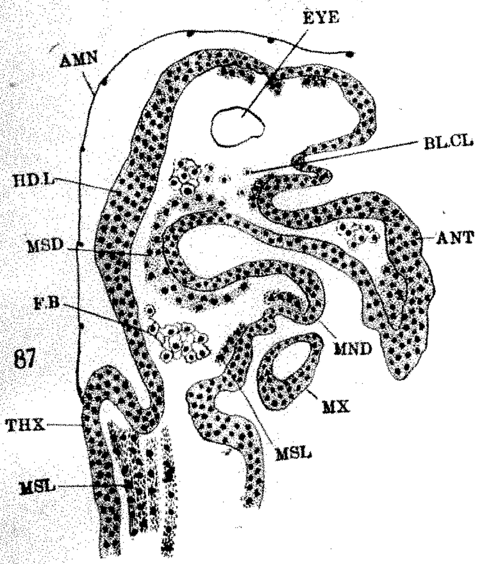
PLATE 16. Fig. 82, 83. L. S. 154 hours stage passing through the anterior end (46 × 8).
Fig. 84. L. S. posterior region (46 × 8).
Fig. 85. T. S. through the abdominal region (46 × 8).
Fig. 86. L. S. posterior end slightly lateral to the mid-ventral line (46 × 8).
All the figures represent 194 hour stage.



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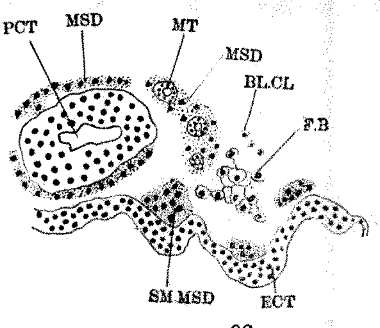

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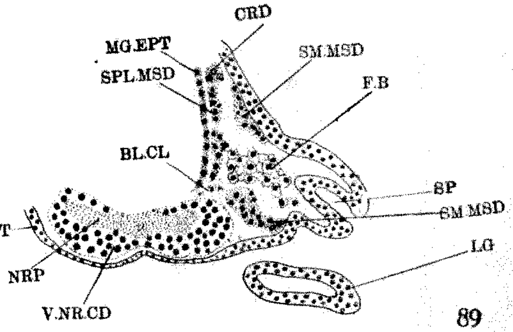

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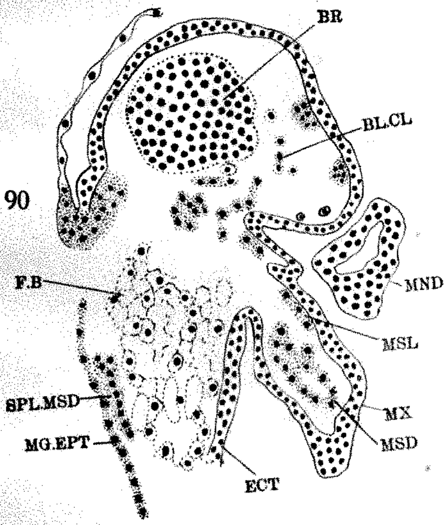

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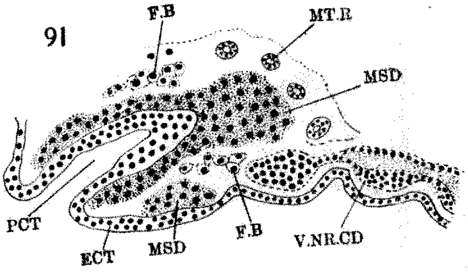

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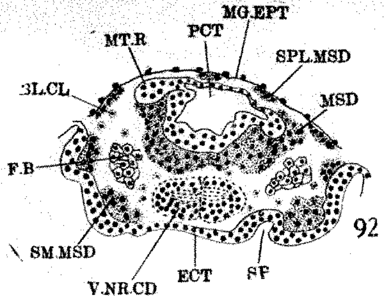
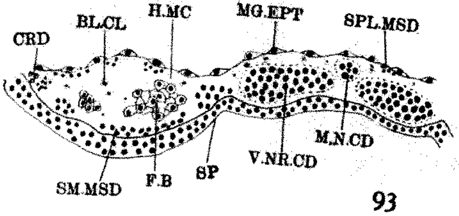
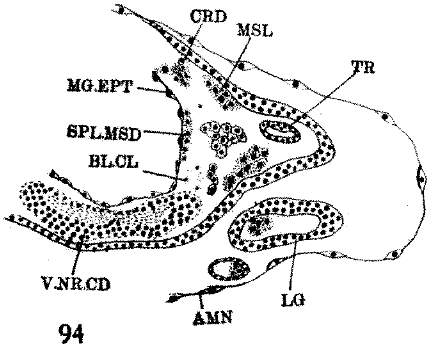
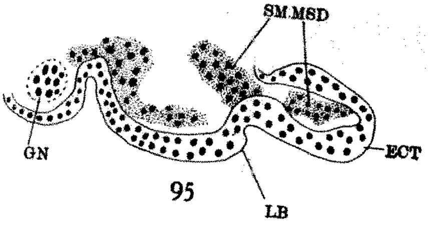
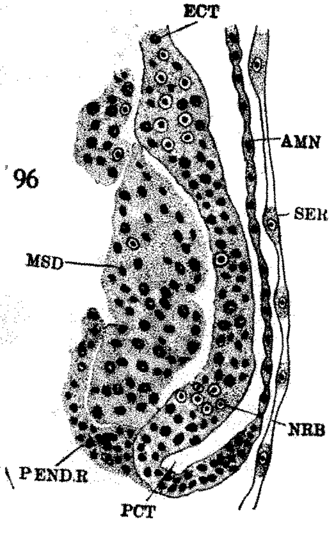
Fig. 89. T. S. thoracic region (46 × 8).
Fig. 90. L. S. through the head region (46 × 8).
Fig. 91. L. S. posterior region passing through the proctodaeum. (46 × 8).
All the figures represent 200 hour stage.











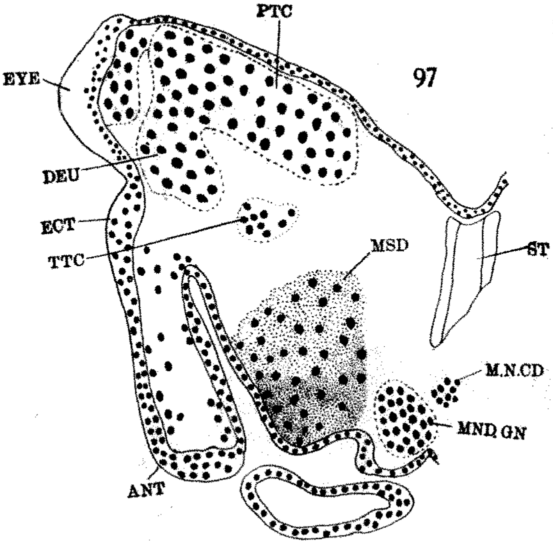


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Fig. 96. L. S. proctodaeum 130 hour stage (46 × 8).
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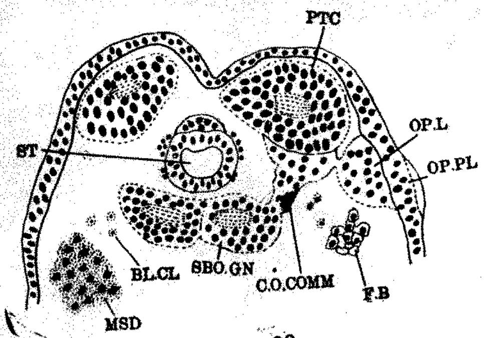

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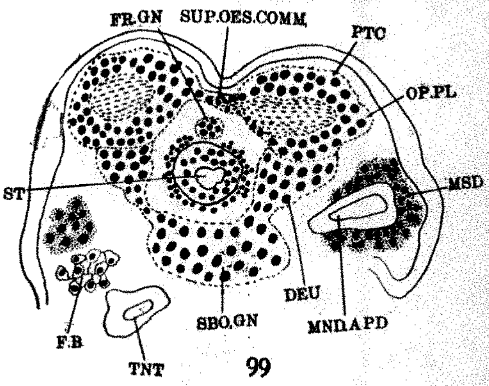

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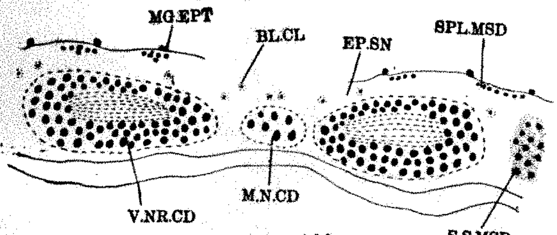

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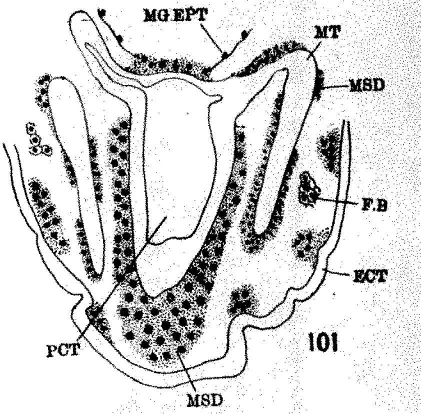

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Fig. 99. Frontal section through the anterior end (46 × 5).

Fig. 100. T. S. through the abdominal region (46x12).

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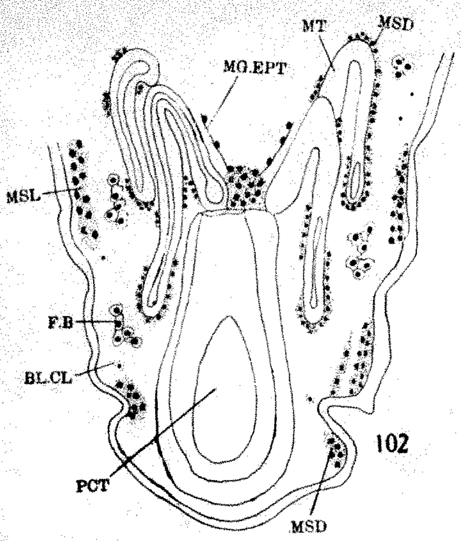

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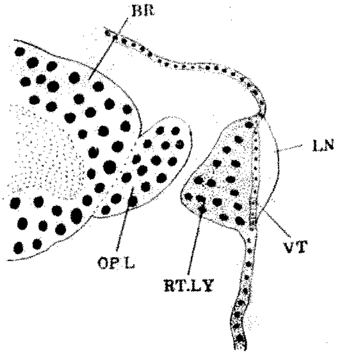

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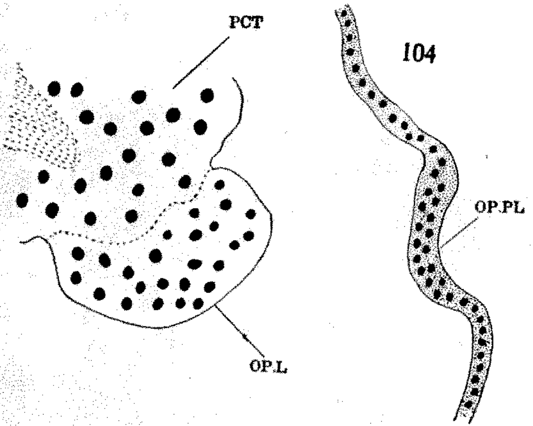

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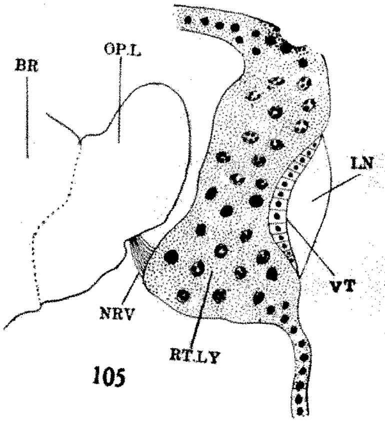

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Fig. 103. Frontal section through the eye (46 × 12).
Fig. 104. Frontal section through the eye (46 × 12).
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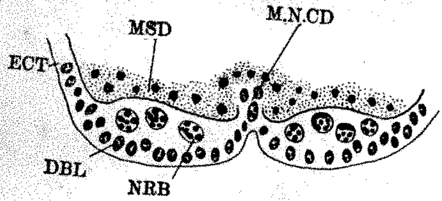
Figures 102, 103 and 105 represent 200 hour stage. Figure 104 represents 180 hour stage.



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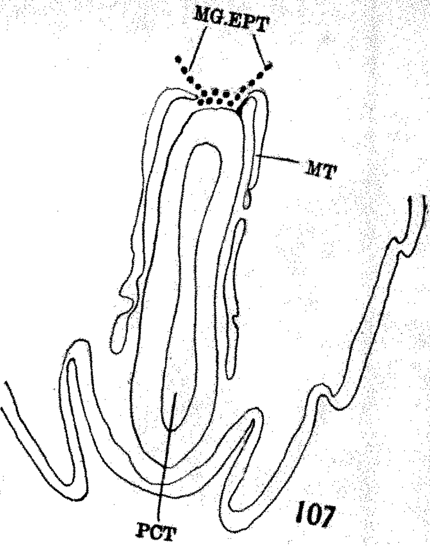

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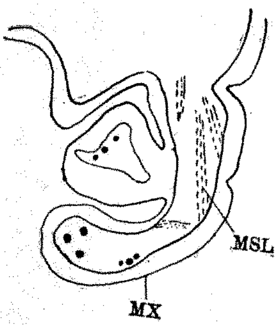

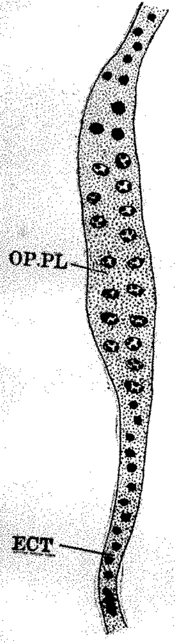

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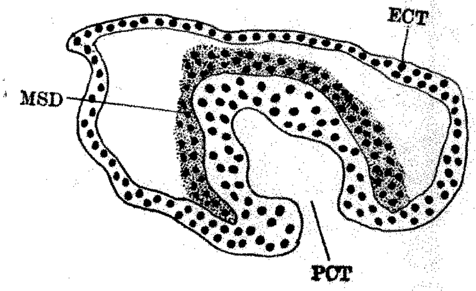

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Fig. 110. Frontal section through the ganthal appendge 282 hour stage (46 × 12; phase contrast)

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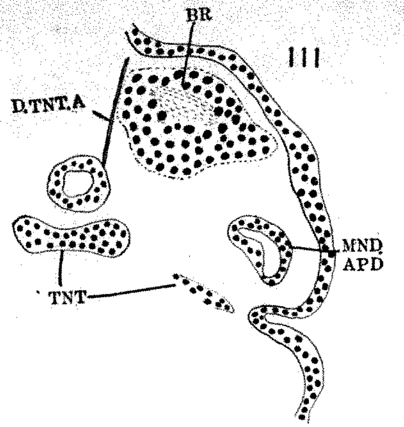

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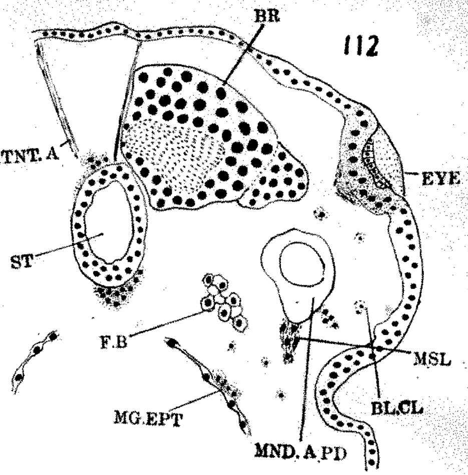

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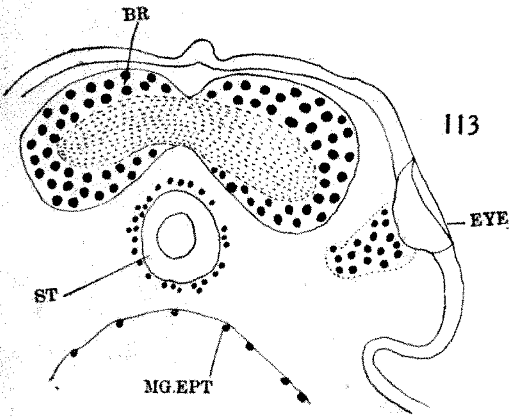

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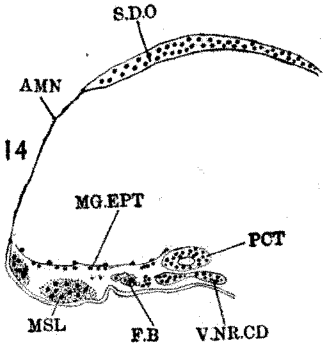

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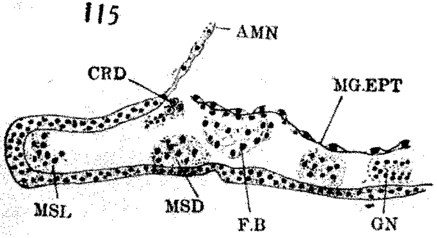

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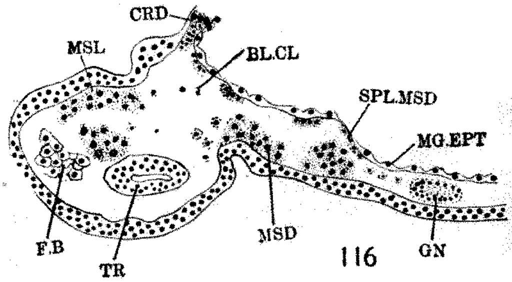

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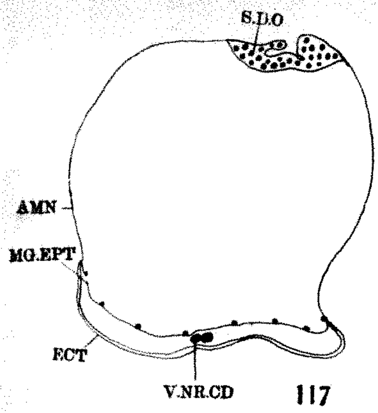

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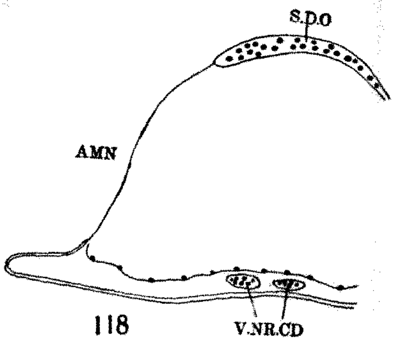

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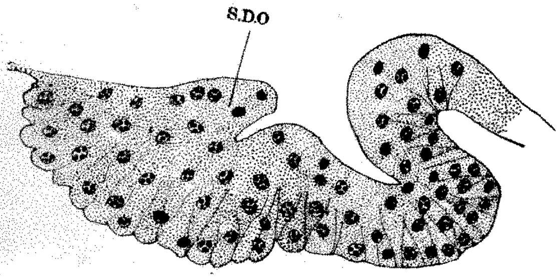

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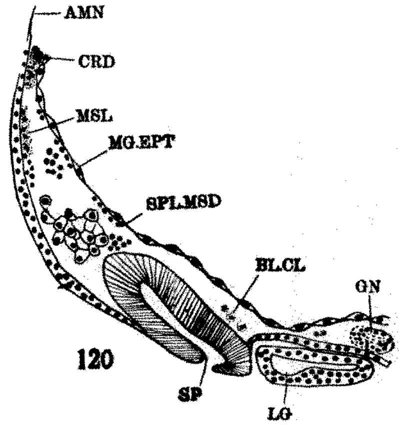

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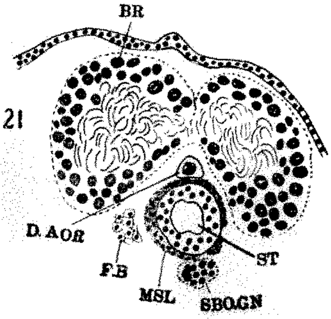

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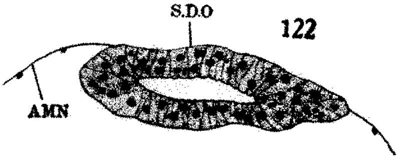

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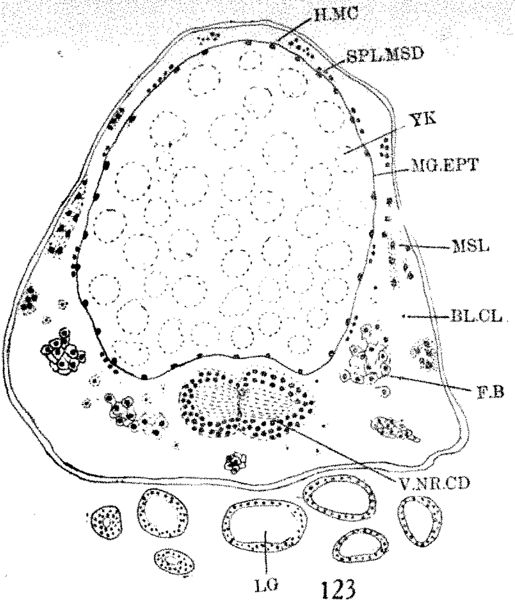

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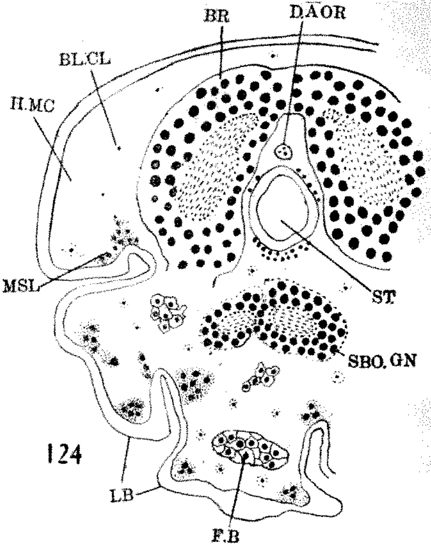

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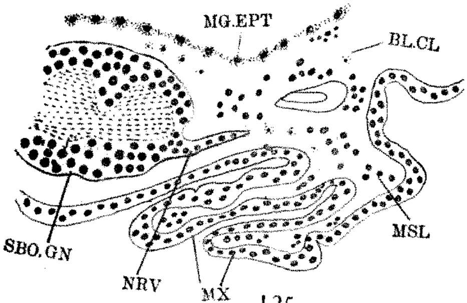

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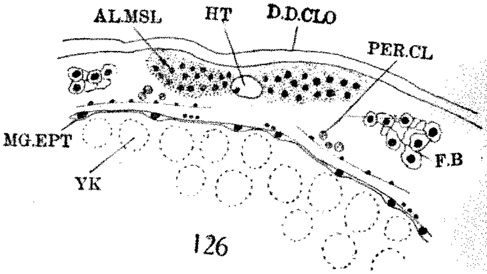

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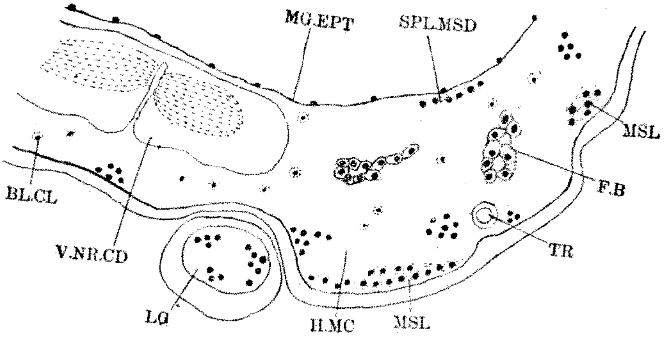

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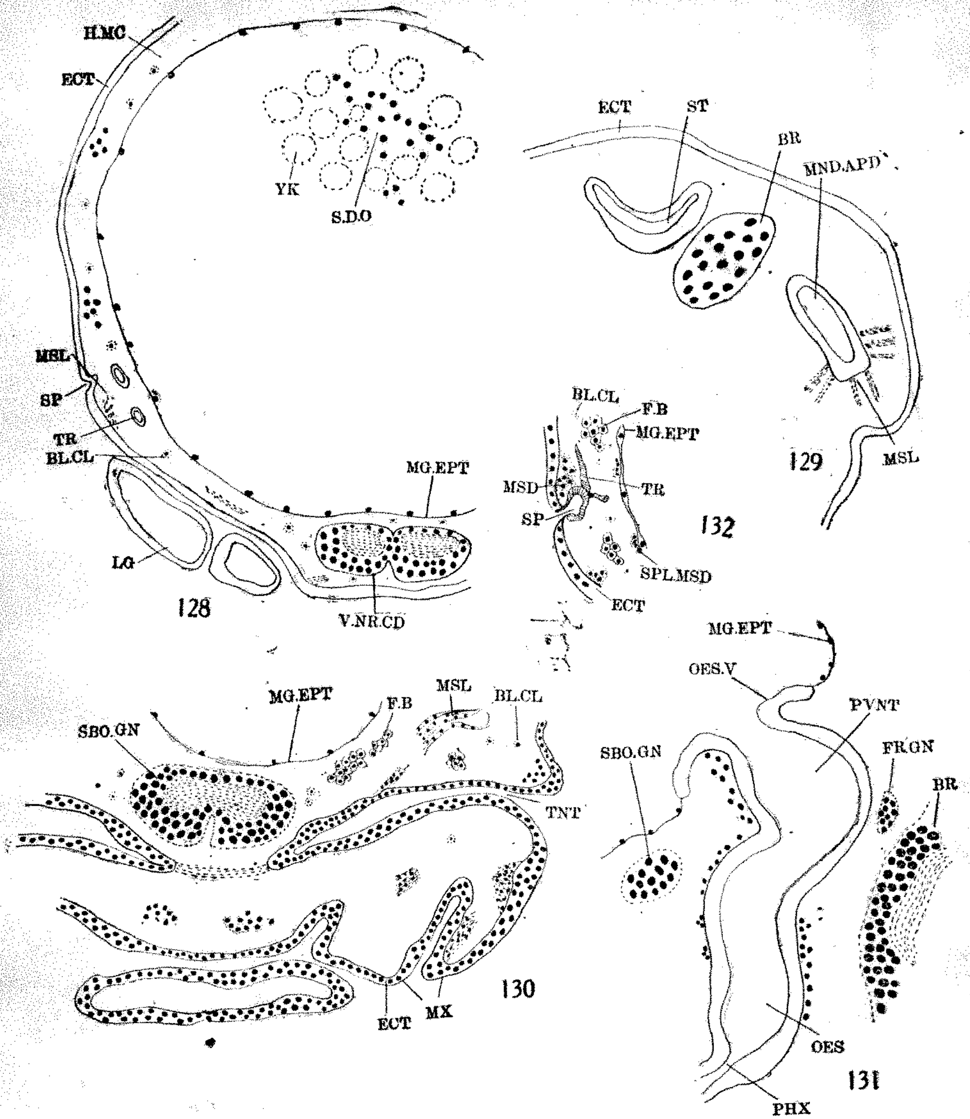

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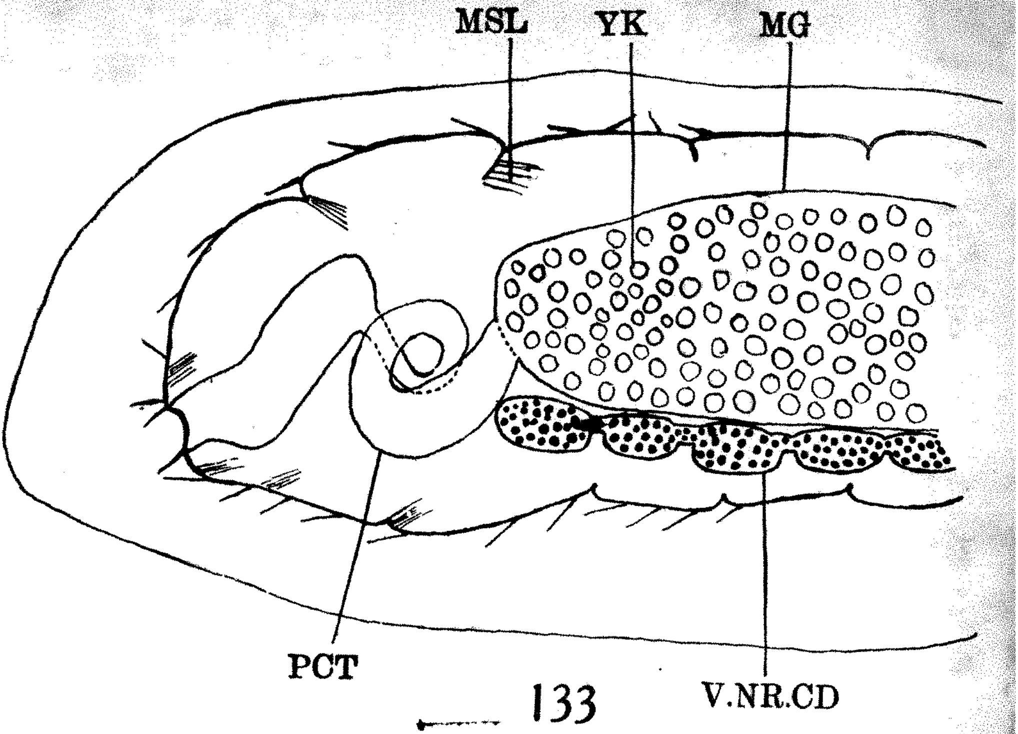

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Plate 26, Fig. 133. Fully developed embryo prior to hatching posterior half showing the ventral nervous system and the coiled hind-gut (46 × 5)·

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Chief Editor

ANATOMY OF THE STEM OF DAEMIA EXTENSA R. Br.†

By N. C. Mukerjee, *Department of Botany, B.R. College, Agra, India.*

Daemia extensa, of the family Asclepiadaceae is a perennial shrub. It is abundant in the upper Gangetic plain and other parts of India, ascending up to 3,000 ft. on the Himalayas. It also extends to Ceylon, Afghanistan, Arabia and tropical Africa[3].

Previous Work

The anatomy of the family Asclepiadaceae has been worked out by several workers. Handa[10] and Singh[17] have studied the activity of the internal cambium, Blaser[2] the latex system, Maheshwari[12], and Singh[17] the location and origin of *internal** and *included* phloem. Sayeedud-Din and Suxena[15] and Sabnis[14] have worked out the general anatomy while the wood structure has been investigated by Baily[1].

Material and Methods

The material for the present study was collected during 1954-55 within the campus of B. R. College, Agra. It was fixed in formalin-acetic-alcohol and Carnoy's fixative and was passed through alcohol-xylol and tertiary butyl alcohol series. Softer material was sectioned at 12-25μ while older pieces were boiled for softening and cut free hand. Safranin-fast green, erythrosine-crystal violet and Delafield's haematoxylin combinations were used for staining.

Anatomy of the young stem

The stem in cross-section is more or less circular in outline. The epidermis consists of a single layer of cells with two types of hairs, glandular and uniseriate. There is a broad cortex of parenchyma with large number of laticiferous cells full of contents. Only a few xylem elements are lignified in the beginning. The pith is very large and is made up of parenchyma cells with numerous laticiferous cells interspersed between them. The presence of *internal* phloem* (Fig. 1) is difficult to make out in cross sections; longitudinal sections however, clearly show it to be of procambial origin.

The cross-section of a thicker stem (Fig 2) shows a few anatomical changes of interest. The outer 3 to 4 layers of cortical cells are collenchymatous while the rest remain parenchymatous with the innermost layer forming a distinct endodermis. The pericycle is broad and has groups of fibres alternating with patches of parenchyma. The walls of these cells are of cellulose as they do not take up safranin and swell up if treated with sulphuric acid. The xylem forms a continuous cylinder and is traversed by narrow lines of parenchyma. These radial parenchyma layers and those of vessels alternate with each other, more or less, in a uniform manner. *Included phloem** is absent.

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† Pergularia extensa N. E. Br.

The most important feature is the occurrence of (Fig. 3) separate strands of *internal phloem** at the periphery of the pith. Large sieve tubes with prominent companion cells are seen, but no internal cambium or fibres could be made out in this region. Pith is broad with abundant laticiferous cells.

CAMBIAL ACTIVITY AND WOOD ANATOMY

The cambium which forms a distinct ring of four or five layers is rather irregular in activity as evidenced by the following peculiarities:

(1) Unequal cambial activity makes the periphery of the wood cylinder wavy (Fig. 6).

(2) Inclusion in the secondary xylem of sometimes quite large areas of ordinary parenchyma (Fig. 4 and 5)

(3) Formation in some cases of a ring of tracheid-like cells at the beginning of the secondary growth. The thickness of this ring varies from place to place. It may be entirely lacking at certain points where the vessels of the secondary wood arise in close contact with the primary xylem (Fig. 3 and 4).

The most characteristic feature of the secondary wood is the arrangement of vessels and secondary xylem rays. The vessels are large and distributed without any definite pattern. They have large alternate pittings.

The rays in the wood do not form radial lines as is seen in the majority of cases, but they are zig-zag running between the vessels and are visible for short distances only. This feature is attributable to the extremely large size of the vessels which disturbs the radial alignment of the rays. A similar case has been reported by Eames and MacDaniels[4] in *Cucurbita.*

The most conspicuous feature, in radial longitudinal section, is the apparent absence of xylem rays (Fig. 8) . This is due to the zig-zag course of the rays. A radial section includes a very small portion of a ray which is not easy to make out; hence it makes the wood appear rayless. Xylem rays are, however, visible (Fig. 7) in tangential longitudinal sections as short, homogenous, uniseriate structures made up of vertically elongated cells.

Periderm is superficial in origin and secondary cortex has no fibre elements. Solereder[16] considers this to be the general rule in the family.

DISCUSSION

The structure of the axis of *Daemia extensa* R. Br. described above conforms with that of the rest of the family in having cellulose fibres in the pericycle, continuous cylinder of xylem and phloem traversed by narrow

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*The committee of Nomenclature (1933) has suggested the use of the term *included* in place of Interxylary and *internal* in place of Intraxylary Phloem. These terms have been used here.

rays, presence of internal phloem and laticiferous cells. The superficial origin of the cork, a well-defined endodermis** and presence of mostly uniseriate hairs, all stress similarity with a general anatomical pattern in the family and suggest close affinities with Apocynaceae.

The most outstanding feature is the irregular cambial activity which is quite usual for many members of the family. In *Daemia*, *Leptadenia*, *Asclepias*, *Ceropegia and Gonolobus* this activity results in the incorporation in the secondary xylem of large unlignified areas. In *Leptadenia*[17], *Ceropegia*, *Asclepias* and *Morrenia* these areas have been stated to be of included phloem while in *Gonolobus*, some other species of *Ceropegia*[13], as well as *Daemia* (present investigation) show that they are parenchymatous. The irregular cambial activity also results, in some cases, in the production of a many cell thick ring of tracheid-like cells. This ring separates the primary xylem from the first-formed vessels in the secondary wood.

Vessels in the secondary wood are very large and not aligned in radial rows. The area occupied by them is very much larger than that occupied by the other elements of the xylem. This is stated to be the general rule in the lianes where mechanical tissues may not be necessary in such large amounts as in arborescent forms. In *Cryptostegia grandiflora*, a well known liana of the family, however, the vessels in the secondary wood are rather, small arranged more or less in radial rows and occupy proportionately a much smaller area in the secondary xylem.

Secondary xylem rays, which are properly visible in the tangential longitudinal sections (Fig. 7) only, are mostly uniseriate and homogenous. This according to Kribs[11] is not a primitive feature but derived from multiseriate condition. These uniseriate rays have also been reported by Blaser[2] in *Cryptostegia*. Barghoorn, as quoted by Metcalfe and Chalk[13], however, thinks that uniseriate rays with high upright cells, may arise in shrubs due to reduced cambial activity and such rays are of a primitive type.

The internal phloem originates from the procambial strands, and separate areas of internal phloem can be clearly made out in very young stem pieces from near the shoot apex. This type of origin of the internal phloem is quite contrary to that described in *Nicotiana* by Esau[7],[8],[9] and in *Leptadenia* by Singh[17]. In *Daemia* there is no evidence of an internal cambium even in very thick pieces of the stem and no new tissues are added to this internal phloem as secondary growth proceeds (Esau[6]). The phloem strands retain their identity even after considerable secondary growth. This is also proved by the undisturbed retention of the protoxylem groups in very thick pieces.

SUMMARY

The stem of *Daemia* possesses the following features of special interest:

1. Presence of grouped unlignified fibres in the pericycle.
2. Primary xylem is in the form of a continuous cylinder.

**Esau[6] states that in certain Asclepiadaceae the primary phloem may be in contact with the cortex, there being no endodermis.

3. Presence of internal phloem is in the form of separate strands at the periphery of the pith and it is primary in origin.

4. Primary xylem cylinder is separated in most cases from the first-formed vessels in the secondary wood by a region of tracheid-like cells over a wide area.

5. Presence of areas of ordinary parenchyma only, in the secondary wood; there is no included phloem.

6. Irregular cambial activity as seen by the formation of included parenchyma and the dented outline of the wood cylinder at its outer periphery.

7. Secondary xylem rays are mostly uniseriate and zig-zag in their alignment.

ACKNOWLEDGMENTS

I am deeply indebted to Prof. Bahadur Singh for suggesting the problem and invaluable guidance received throughout the course of this investigation. I am also extremely grateful to Principal R.K. Singh for facilities and encouragement. My thanks are also due to Prof. M.S. Mani of St. John's College, Agra for taking these microphotographs.

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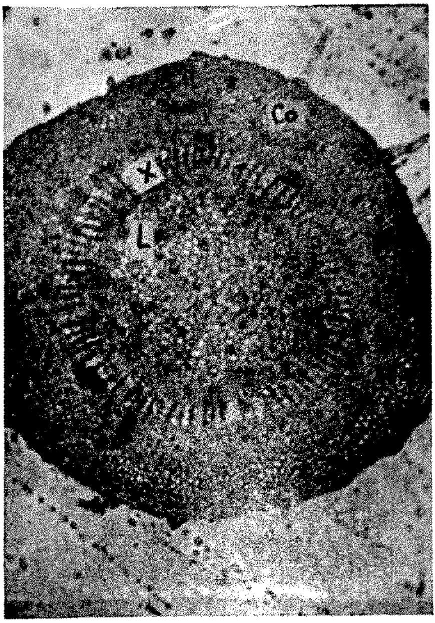

Fig. 1

T. S. stem (very young). Note the absence of fibres in the inner periphery of the cortex (Co), a continuous xylem cylinder (X) and the large number of latex-containing cells (L) in the pith.

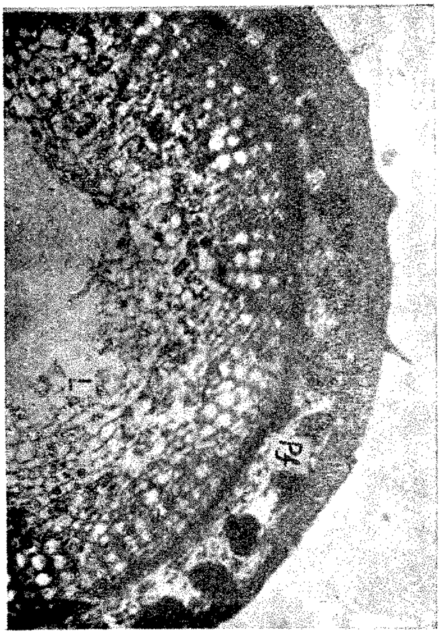

Fig. 2

S. T. of a young stem; note the groups of pericyclic fibres (PF) and large number of latex containing cells in the pith (L)

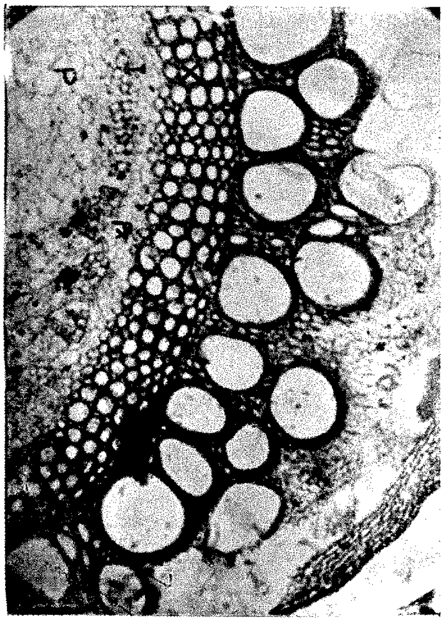

Fig. 3

T. S. Stem. Showing the first-formed secondary wood. X- primary xylem, I- internal phloem, P-Pith; PX undisturbed protoxylem

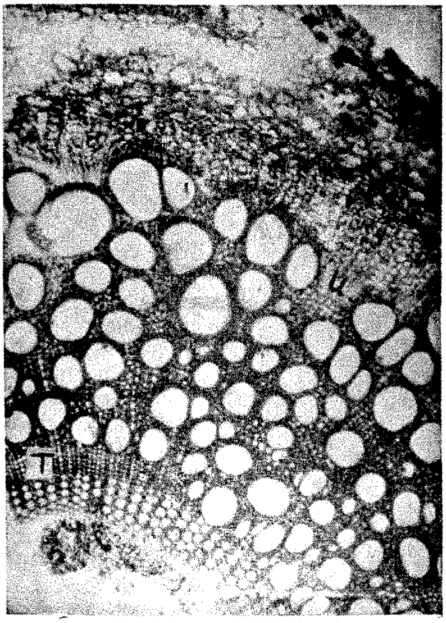

Fig. 4

T. S. thick stem, Note the irregular cambial activity; a newly formed large area of unlignified xylem (U) and the tracheid like (T) elements that separate the primary xylem from the secondary xylem at some places.

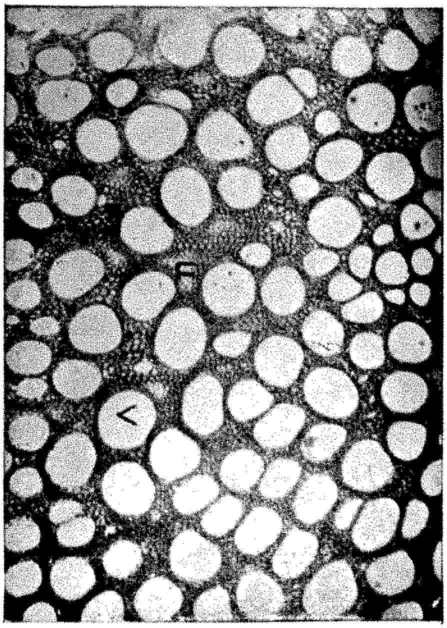

Fig. 5

T. S. mature wood; note the large size of vessels (V) unlignified xylem (U) and the apparent absence of wood rays.

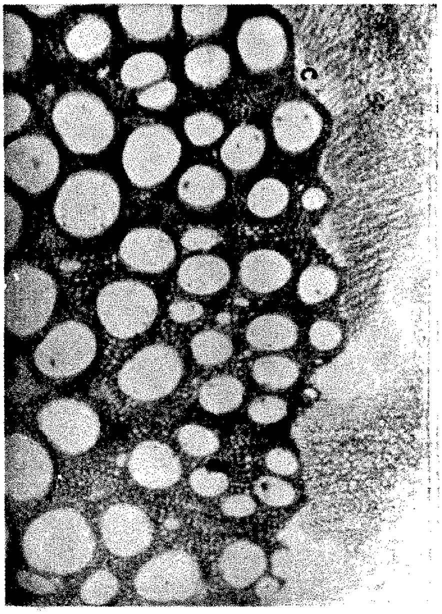

Fig. 6

T. S. thick stem. Note the zig-zag cambium ring (C) and the absence of fibre elements from in the secondary cortex. (SC).

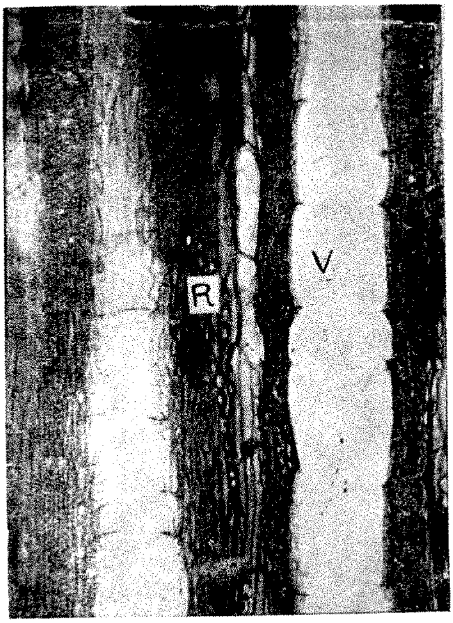

Fig. 7

Tangential longitudinal section of a thick piece of stem. Note t large vessels (V) and Uniseriate rays (R).

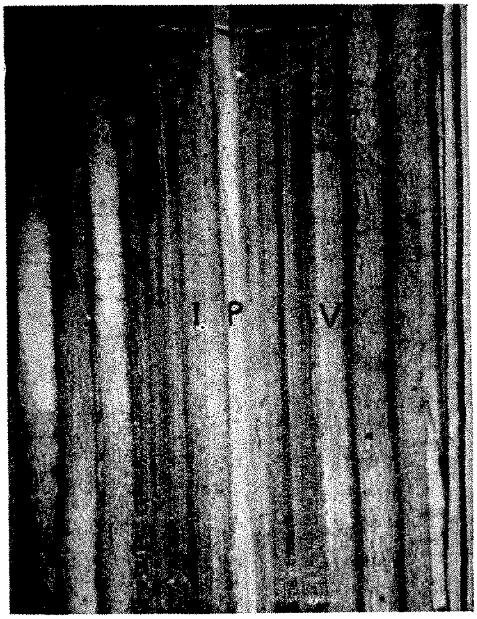

Fig. 8

Radial longitudinal section of thick stem. Note the absence of rays in the section. V Vessel, P-Pith, I- internal phloem.

INCIDENCE OF SEEDLING-ROT, ROOT-ROT, AND WILT OF *CYAMOPSIS PSORALIOIDES* UNDER MANURED AND UNMANURED CONDITIONS

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In the western districts of Uttar Pradesh the 'guar' (*Cyamopsis psoralioides* DC.) crop is usually taken after potato, without subsequent manuring, in order to get green fodder during May and June. The *Cyamopsis* plants live on the residual effects of the heavy doses of the manure applied to the preceding potato crop. In other localities, however, sometimes a light manuring is done to raise a good fodder crop. It has been noticed that the incidence of mortality in *Cyamopsis psoralioides*, caused by *Rhizoctonia solani* Kuhn. and *Fusarium coeruleum* (Lib) Sacc,. as reported earlier (7), varies according to the manure-content of the soil in the fields.

Manuring may favourably influence the incidence of the disease by providing a direct nutrient medium for the growth of R. *solani* and *F. coeruleum,* associated with seedling-rot, root-rot, and wilt of *Cyamopsis psoralioides*, or may adversely reduce the disease by creating a favourable nutritive condition for a vigorous growth of the guar' plants It may also enhance the growth of micro-organisms, antagonistic to *R. solani* and *F..coeruleum,* in the soil and thereby affect the incidence of the disease.

In order to test either of the possibilities of the effects of manuring on the incidence of mortality in *Cyamopsis*, the experiments detailed on the following ages were carried out during 1949-51.

Experimental Methods and Results

The pot experiments consisted of six replications for each treatment The pots were filledwith autoclaved soil and were manured or left unmanured. The manure was added after autoclaving the soil at the rate of one pound per pot containing approximately 10 pounds of soil. The soil in pots was inoculated by thoroughly mixing mycelial and sclerotial growth of *R. solani* scrapped from agar plates or with spore suspension of *F. coeruleum,* as the case may be Twenty seeds were sown in each pot. The experiment was run in three series, one for *R. solani,* the other for *F. coeruleum,* and the third for mixed inoculum of the two fungi (Table 1).

The field plan for the experiments consisted of four replications for each treatment. Manured beds were given well decompsed farm-yard-manure at the rate of six cartloads (about 60 maunds per acre). The crop was sown in rows, 8-feet long and 2-feet apart, in order to facilitate observations. The soil in rows was inoculated with cultures of *R. solani* and *F. coeruelum* separately.

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This inoculum was added in addition to the natural inoculum already existing in the soil. One hundred seeds of 'guar' were sown in each row. The observations were recorded twice a week (Table 2).

Table 1

Disease-incidence in 'guar' sonw in soil inoculated with *R. solani* and *F. coeruleum* under manured and unmanured conditions. Pot experiments.

		Disease Incidence (p.c.)			
Fungus	Treatment	Percentage of Emergence	Seedling rot	Root-rot and wilt	Total
		Year 1949			
R. solani	Manured	40.0	59.0	27.0	86.0
	Unmanured	41.5	62.5	29.5	92.0
F. coeruleum	Manured	89.0	6.0	64.0	70.0
	Unmanured	84.0	10.0	80.0	90.0
R. solani &	Manured	49.0	56.8	30.0	86.8
F. coeruleum	Unmanured	53.0	60.5	33.8	94.3
	C.D. at 5%	6.4	4.8	2.0	4.7
		Year 1950			
R. solani	Manured	43.8	51.2	31.7	82.9
	Unmanured	44.0	50.0	38.6	88.6
F. coeruleum	Manured	100.0	13.2	46.3	59.5
	Unmanured	96.2	14.8	61.0	75.8
R. solani	Manured	53.8	48.9	49.5	97.4
F. coeruleum	Unmanured	40.0	50.0	50.0	10.0
	C.D. at 5%	8.6	3.9	1.5	4.0

Table 2

Disease incidence in 'guar' sown in soil inoculated with *R. solani* and and *F. coeruleum* under manured and umnanured conditions (Field Experiments).

		Disease-Incidence (Percent)			
Fungus	Treatment	Percentage of emergence	Seedling rot	Root-rot and Wilt	Total
		Year 1949			
R. solani	Manured	69.0	23.0	14.0	37.0
	Unmanured	63.0	22.8	20.9	43.7
F. coeruleum	Manured	93.0	12.5	8.0	20.5
	Unmanured	90.0	14.0	13.6	27.6
	C.D. at 5%	8.2	3.1	2.6	4.0

		Year 1950			
R. solani	Manured	51.9	20.0	12.5	32.5
	Unmanured	51.0	21.3	19.5	40.8
F.coeruleum	Manured	89.9	17.6	14.6	32.2
	Unmanured	85.7	17.9	21.6	39.5
	C.D. at 5%	6.6	4.1	1.9	3.7

These results have indicated that in the case of *R. solani* emergence of *Cyamopsis* seedlings is equally affected in manured and unmanured soils. The incidence of post-emergence seedling-rot is also high and identical under manured and unmanured conditions. However, there is significant increase in the occurrence of root-rot and wilt of adult plants in unmanured soil in comparison to that in manured soil. Consequently, the figures for total mortality show a significant difference between the two treatments with soil inoculated with *R. solani.* Under identical itensity of post-and pre-emergence seedlig rot a difference in the mortality of adult plants suggests that the difference are due to better nutritive conditions provided by manuring resulting in increased vigour of the plants and their tissue maturity. Had there been any antagonistic effect against *R. solani* in the manured soil the incidence of seedling-mortality shuld have been significantly different in the two treatments. This has been further supported by field observations showing that in manured plots recovery amongst diseased plants, after they had suffered slight damage, was better than in unmanured plots.

Emergence of seedlings in soil inoculated with *F. coeruleum* is nearly perfect in both manured and unmanured series. The seedling-rot has been relatively moderate in fields and very low in pots. This is apparently due to this fungus not being the major cause of seedling-rot of *Cyamopsis.* There is no significant difference between the figures for seedling-rot by *F. coeruleum* in manured and unmanured series. The death of adult plants due wilt has been considerably lower in manured plots than in unmanured plots. Whether this significant difference is due to plant vigour or due to some antagonistic activity in the manured soil, inhibiting the growth of *F. coeruleum,* is not clear from this experiment as the fungus has not been found to cause severe seedling-rot and there is not consistency in the results for seedling-rot during the different years.

The results from mixed inoculum of the two fungi are similar to those obtained with *R. solani* which usually predominates if present with *F. coereuleum.* The two fungi combined together mostly cause hundred present mortality of the *Cyamopsis* plants in pots.

Further experiments were carried out during 1950-51 to get more informaion about the mode of action of manures in reducing mortality in *Cyamopsisi.* These experiments were carried out under artificial conditions to test the virulence of *R. solani* and *F. coeruleum* in the absence or presence of normal microbilogical activities in the unmanured and manured soils. Variously treated soil* was filled in pots and surface disinfected seeds of *Cyamopsis psoralioides* were planted after inoculation of the soil with one month old cultures of *R. solani* and *F. coeruleum* separately (Tables 3 and 4).

Table 3

Seedling-emergence and subsequent mortality of. 'guar' in variouly treated soil inoculated with *R. solani*

Treatment of the soil		Percentage Emergence	Percentage of mortality		
			Seedling rot	Root-rot of adult plants	Total
		Year 1950			
Unmanured	autoclaved	58.0	58.2	38.3	96.5
	Unautoclaved	60.0	59.9	36.9	96.8
	C.D. at 5%	2.8	1.9	4.2	6.1
Manured	autoclaved	60.6	43.4	25.5	68.9
	Unautoclaved	64.0	46.0	23.5	69.9
	C.D. at 5%	3.9	4.2	3.5	5.0
		Year 1951			
Unmanured	Autoclaved	66.5	51.5	29.8	81.3
	Unautoclaved	65.8	50.0	28.5	78.5
	C.D. at 5%	3.1	2.2	5.8	4.7
Manured	Autoclaved	64.0	44.8	20.8	65.6
	Unautoclaved	63.0	44.2	21.2	65.4
	C.D. at 5%	4.2	3.1	3.0	6.1

Table 4

Seedling-emergence and subsequent mortality of 'guar' plants in variously treated soils inoculated with *F. coeruleum*

Treatment of the soil		Percentage of emergence	*Percentage of Mortality*		
			Seedling rot	Wilt of adult plants	Total
		Year 1950			
Unmanured	autoclaved	96.8	4.8	69.8	73.8
	Unautoclaved	96.0	2.7	37.6	40.3
	C. D. at 5%	1.6	1.2	5.2	8.2
Manured	autoclaved	96.4	8.2	51.7	59.9
	unautoclaved	100.0	5.9	30.5	36.4
	C. D. at 5%	3.0	2.1	4.6	4.8

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*The treatment of the soil were as follows :

1. Unautoclaved soil and fungus culture
2. Autoclaved soil and fungus culture
3. Autoclaved soil, manure. and fungus culture
4. Unautoclaved soil, manure anb fungs culture

The manure was added before steaming of the soil.

Year 1951

Unmanured	autoclaved	98.0	8.2	54.2	62.4
	unautoclaved	96.0	5.4	30.9	36.3
	C. D. at 5%	1.7	2.5	6.4	5.4
Manured:	autoclaved	100.0	6.2	43.5	49.7
	uhautoclaved	100.0	5.0	21.0	26.0
	C. D. at 5%	2.0	1.0	3.0	4.8

The mortality due to *R. solani* (Table 3) is lower in manured series than in unmanured series. Except this difference there is absolutelyno other influence of the various treatments. The sterlilization of the manured or unmanured soil has produced no effect on the mortality in the respective series. It was presumed that autoclaving will deter the microbiological activities in the soil while autoclaved manured soil will provide a more nutritive medium for the vigorous growth of plants than unmanured autoclaved soil. On the other hand unautoclaved manured oru nmanured soil may be rich in microflora which may create unfavourable conditions for the growth of the fungus. However, from the results (Table 3) it is indicated that even in unsterilized soil the mortality is as heavy as in sterilized soil provided there is no nutritive condition for vigorous growth of the plants. At the same time the mortality has been almost identically lowered both in autoclaved as well as unautoclaved soils if manure has been added to them. This suggests that the reduced mortality due to *R. solani* in manured soils in comparison to unmanured soil is due to plant vigour and not due to antagonism of soil microflora under the conditions of the experiments conducted here.

Further experiments are required "on the effects of associated microflora on the parasitism of *R. solani* isolated from *Cyamopsis psoralioides*" in order to arrive at any final conclusion. Some preliminary work carried out with the bacterial and fungal isolates obtained from the soil in manured pots used in these experiments. It has been observed (Pl. 1 Fig. 2) that *R. solani* soon overcomes the growth of bacteria and molds and in late stages its sclerotia have been seen scattered even on the bacterial colonies.

In the case of *F. coeruleum* also the mortality in manured series has been lower than in unmanured series. But here the difference occur within the series also, showing an increased incidence on mortality in autoclaved soil than in unautoclaved soil. Even in manured series, where the plant vigour was better than in unmanured series, the soil autoclaving has increased the percentage of plants killed. From these results it is, therefore, evident that the reduced loss from *F. coeruleum* in manured soils is primarily due to some antagonistic action against this fuhgus. Plant vigour also helps in lowering the mortality as is evident from the data for manured and unmanured autoclaved soil. In both these treatments the autoclaving of the soil can be presumed to have diminished the soil microbiological activities, yet the rate of mortality is lower in manured soil than in unmanured soil.

As has been mentioned for *R. solani* this fungus was laso grown in Petri-dishes along with bacterial and fungal isolates obtained from manured soil in pots used in the above experiments. The growth of *F.coeruleum* is completely inhibited by almost all the organisms tried (Pl. 1, Fig. 1).

DISCUSSION AND CONCLUSIONS.

Application of manures is known to increase resistance in plants through plant vigour as a result of nutritive effects of the manure and also to reduce incidence of disease through soil microbial antagonism, although there are instances when the presence of organic matter in the soil increases the incidence of the disease and prevalence of a soil-borne plant pathogen through favourable nutritive effect on the latter.

Of late much attention has been paid to 'biological control of soil-borne diseases by application of fresh organic matter to the soil. It is assumed that increased activity of the saprophytes developing on the fresh organic matter must occur at the expene of, and to the detriment of, plant parasites. This phenomenon of microbiological antagonism has been discussed in detail by Fawcett (1), Garrett (2,3) Waksman (8, 9), and Sanford (4, 5, 6). In the case of seedling-rot, root-rot, and wilt of *Cyamopsis psoralioides*, caused by *R. solani* and *F. coeruleum*, it has been found that both these fungi cause less damage in manured soil than in unmanured soil. The preliminary experiments carried out in this connection have, however, indicate the possibility that this reduced disease incidence might not be solely due to microbial antagonism in the soil. Plant vigour under manured conditions also plays some role in reducing the infection by *R. solani*. However, in the case of *F. coruleum* there are definite indications that reduced appearance of wilt in manured soils is due to the presence of antagonistic organisms in the soil.

SUMMARY

Under manured conditions the incidence of seedling-rot, root-rot, and wilt of *Cyamopsis psoralioides* DC., caused by *Rhizoctonia solani* Kuhn. and *Fusarium coeruleum* (Lib.) Sec., is considerably reduced. There are indications that the plant vigour, resulting from the high nutritive status of the manured soil, is the chief cause of reduction in infection by *R. solani*. At the same time, the reduced mortality due to *F. coeruleum* is definitely due to soil microbial antagonism.

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EXPLANATION OF PLATES

PLATE I

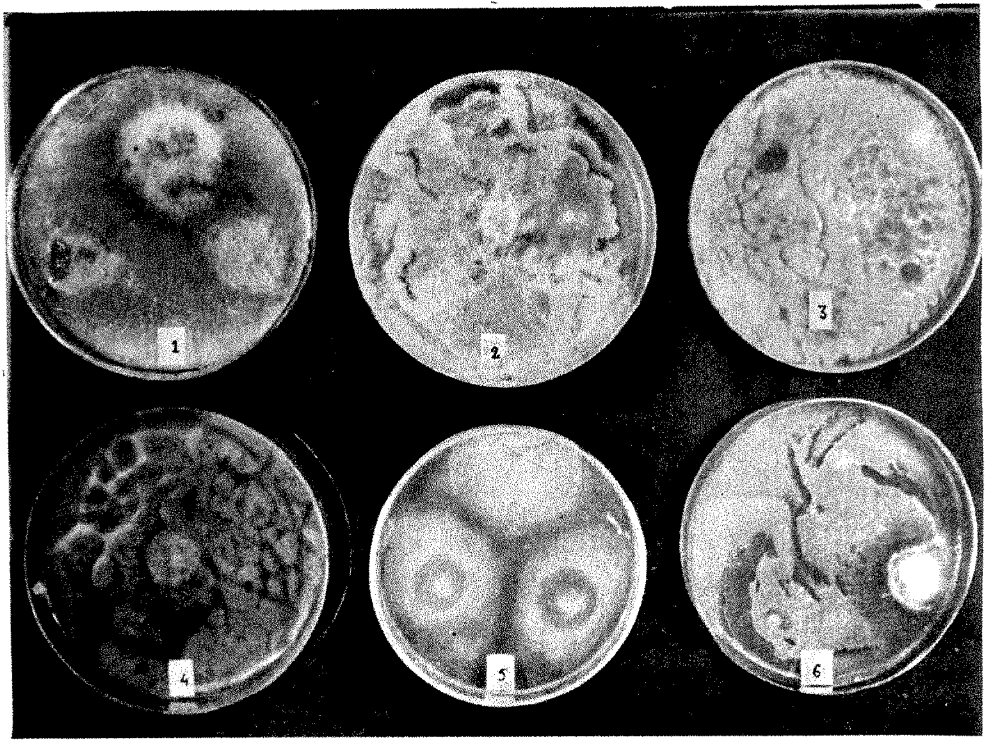

Fig. I Growth of *F. coeruleum* in presence of some moulds and bacteria obtained from infected soil.

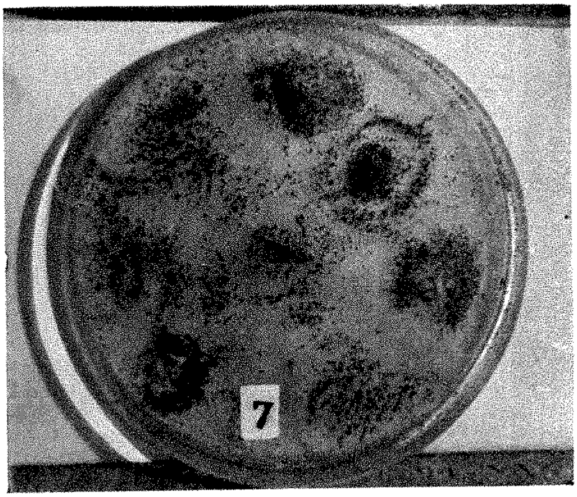

Fig. 2. Growth of *R. solani* in presence of some moulds and bacteria obtained from infected soil.

THE SECOND CONTRIBUTION TO THE STUDY OF FUNGI FROM AJMER (RAJASTHAN)

By N. C. Joshi, *Botany Department, Government College, Ajmer.*

Joshi (1957) described some 55 Fungi both pathogenic and nonpathogenic on different hosts from Ajmer. Some more Fungi have been identified after the first paper was sent to press. All the collections have been kept in the Mycology herberium of the Botany Department, Government College, Ajmer and some important ones have been deposited at the Common wealth Mycological Institute England and Herb. Crypt. Indiae. Orient, New Delhi.

The Fungi have been arranged in the subgroups of Phycomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes.

Phycomycetes

56. *Albugo candidus* (Pers) Leville (Saccardo 1888, Butler & Bisby 1931) On the living leaves of *Cleome viscosa*, Govt. College campus, 6-10-1956, Leg. N.C.J., (conidial stage); of *Gynandropsis pentaphylla* D.C., Government College campus, 19-10-56, Leg. N. C. J., (conidial stage).
57. *Peronospora trigonella* Gaumann (Mundkur 1938). On the living leaves of *Trigonella foenum-graecum* L., Sadapura, 28-2-57, Leg. N.C.J., (conidial stage).
58. *Peronospora meliloti* Syd. (Mundkur 1938). On the living leaves of *Melilotus* Sp., Manoharpura, 28-2-57, Leg. N.C.J., (Conidial stage).

Ascomycetes

59. *Capnodium eugeniarum* CKE (Saccardo 1882; Butler & Bisby 1931). On the living leaves of *Eugenia jambalana*, Civil lines, 7-10-56, Leg. N.C.J., (Asexual and Sexual stage).
60. *Capnodium anonae* Patouill (Saccardo 1905; Butler & Bisby 1931). On the living leaves and twigs of *Ficus benghalensis*, Jwaja, Leg. N.C.J., (Sexual stage only).
61. *Capnodium citri* Berk & Desm (Mundkur 1938). On the living leaves and fruits of *Citrus* Sp., Pushkar, 8-10-5, Leg. N. C. J., (Sexual stage).
62. *Erysiphe polygoni* D.C. (Chona & Munjal 1955). On the living leaves, fruits and twigs of *Tephrosia purpuria*, Civil lines, 9-1-57, (Perithecial and conidial stages).

63. *Meliola tamarindi* Syd. (Saccardo 1928; Butler & Bisby 1931). On the living leaves of *Tamarindus indica* L., Pushkar, 5-11-56, Leg. N. C. J., (Sexual stage).

64. *Meliola mangiferae* Earl. (Saccardo 1913, Butler & Bisby 1931) On the living leaves of *Mangifera indica* L., Happy valley, 16-10-56, Leg. N.C.J., (Sexual stage).

65. *Meliola psidii* Fries (Saccardo 1882 ; Mundkur 1938). On the living leaves and fruits of *Psidium guyava.*, Pushkar, 13-1-56, Leg. N.C.J., (Sexual stage).

66. *Meliola carissae* Doidge (Mundkur 1938). On the living leaves of *Carissa carandas* L., Pushkar, 10-4-56, Leg. N.C.J., (Sexual stage).

67. *Meliola sacchari* Syd. (Saccardo 1928). On the living leaves of *Saccharum officinarum* L., Pushkar, 11-11-56. Leg. N.C.J., (Sexual stage).

68. *Phyllachora sacchari* P. Henn. (Saccardo 1897). On the living leaves of *Saccharum spontaneum*, Pushkar, 6-11-56, Leg. N.C. J., (Perithecial stage).

69. *Phyllachora graminis* (Pers) Fekl (Saccardo 1883). On the living leaves of *Andropogon* Sp., Chamunda, Leg. N. C. J., 6-11-56, (Perithecial stage).

BASIDIOMYCETES—

70. *Melanotaenium brachiariae* Viegas (Mundkur & Thirumalachar 1951). On the living leaves of *Brachiaria distachya* (L) Haines, Nasirabad Ghati, 7-1-57, Leg. N. C. J.

71. *Tilletia eleusines* Syd. (Mundkur & Thirumalachar 1951). In the oavries of *Eleusine aegyptiaca* Desf, Pushkar, 13-1-57, Leg. N.C.J.

72. *Cintractia cyperi* Clinton (Mundkur & Thirumalachar 1951). In the spikelets and peduncle of *Cyperus* Sp., Todgargh, 10-9-56, Leg. N.C.J.

73. *Ustilago crus-galli* Tracy & Earl (Mundkur & Thirumalachar 1951). In the inflorescence of *Echinochloa frumentacea* (Roxb.) Link, Todgragh, 11-9-56, Leg. N. C. J.

74. *Puccinia cynodontis* Desm (Saccardo 1888; Butler & Bisby 1931). On the living leaves of *Cynodon dactylon*, Adarsh nagar, 20-1-57, Leg. N. C. J., (Uredial and Telial stages).

75. *Uromyces andropogonis* Syd. (Saccardo 1912; Butler & Bisby 1931). On the living leaves of *Andropogon* Sp., Annasagar Lake, 8-10-56, Leg. Chatumal, (Uredial and Telial stages).

DEUTEROMYCETES—

76. *Alternaria brassicae* (Berk) Balle (Saccardo 1886; Butler & Bisby 1931). On the living leaves of *Brassica campestris* L. Adarshnagar, 2-3-56, Leg. N. C. J.

77. *Fusarium oxysporum* sensu Synder & Hansen (Joshi & Agnihotri 1956). In the living roots and stem of *Cuminum cyminum* L., Kekri, 2-2-56, Leg. J. P. A.

78. *Helminthosporium gramineum* Rabenh (Saccardo 1892; Butler Bisby 1931). On the living leaves of Hordeum vulgare L., Puskar, 11-2-57, Leg. N.C.J.

79. *Cercospora leucosticta* Ell. & Ev. (Mundkur 1938). On the living leaves of *Melia azadirachta*, Pushkar, 11-1-57, Leg. N.C.J.

80. *Cercospora euphorbiae* Kellerm & Single (Butler & Bisby 1931). On the living leaves of *Euphorbia nibuliae*, Foysagar, 13-9-56, Leg. N. C. J.

81. *Cercospora calotropidis* Ell. & Ev. (Butler & Bisby 1931). On the living leaves of *Calotropis gigantea* Ait, Civil lines, 10-4-56, Leg. N. C. J.

82. *Cercospora sesami* Zimm (Saccardo 1906). On the living leaves of *Sessamum indicum* L., Pushkar, 7-10-56, Leg. N.C.J.

83. *Colletotrichum indicum* Dastur (Mundkur 1938). On th living bracts, bolls and seeds of *Gossypium* Sp. Pushkar, 17-1-57, Leg. N.C.J.

84. *Gloeosporium raciborski* P. Henn. (Mundkur 1938). On the living leaves of *Mangifera indica* L., Happy valley, 3-1-56, Leg. N. C. J.

85. *Oidium mangiferae* Berthet (Mundkur 1938). On the inflorescence of *Mangifera indica* L., Happy valley, 3-4-56, Leg. N.C.J.

ACKNOWLEDGEMENT

I am grateful to the Director, Commonwealth Mycological Institute England for the help in the identification of some of the Fungi and to Mr. M.B. Raizada for identifying some hosts. My thanks are due to Dr. M. J. Thirumalachar, Principal Bhim Sen and Prof. B. Tiagi for inspiration.

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OBSERVATIONS ON SPORE GERMINATION OF SPHACELOTHECA MCALPINEAE ZUNDEL ON HETEROPOGON CONTORTUS L.

By N. C. Joshi, *Department of Botany, Government College, Ajmer.*

Sphacelotheca mcalpineae Zundel has been reported (Joshi 1955) to occur on *Heteropogon contortus* L near Ajmer. The spores of the smut readily germinate in water and solutions of various sugars, but a number of salts proved to be toxic. The present paper embodies results of the above observations.

Results

Effect of Salts—Sodium chloride and sodium carbonate were too toxic and no germination was obtained even in 0.1% solution of the salts. Ammonium sulphate and potassium chloride also proved to be highly toxic. The other salts such as potassium sulphate, magnesium sulphate, potassium nitrate and potassium phosphate were not so toxic although the germination percentage remained fairly low. The results of these germination studies are shown in Fig. 1.

Effect of Sugars—In order to determine the effect of sugars the spores were germinated in 5% solutions of dextrose, levulose, maltose, lactose sucrose and malt extract. Best germination was obtained in lactose as shown in Fig. 2.

Effects of Hydrogen ion Concentration—Further observations were made on the effect of pH when the spores were germinated in 5% lactose solution at room temperature (22°to 24°C.) having a pH range of 1.5 to 10.5 which was determined by Beckman's pH meter The results as given in Fig. 3 show that the spore are capable of germination in a wide range of pH, i. e. 2.0 to 10.0, the optimum germination being at pH 6, while there was no germination at 1.5 and 10.5.

Summary

Observations on the effect of different salts, sugars and pH on the germination of the spores of *Sphacelotheca mcalpineae* Zundel have been made.

Literature Cited—

Joshi. N. C. (1955). Occurrence of *Sphacelotheca mcalpineae* Zundel on
Heteropogen Contortus L
Curr. Sci., Vol. 24, 62-63.

Acknowledgement

I am grateful to Dr. M. J. Thirumalachar for the identification of the fungus and his encouragement. My thanks are also due to Principal, V. V. John and Prof. B. Tiagi for facilities.

Text Figures 1 to 3.

Fig. 1. Graphs showing the % germination of the spores in various concentrations of different salts.

Fig, 2. Diagram showing the % germination of spores in different sugars.

Fig, 3. Graph showing the % germination of the spores at different pH.

Fig. 1.

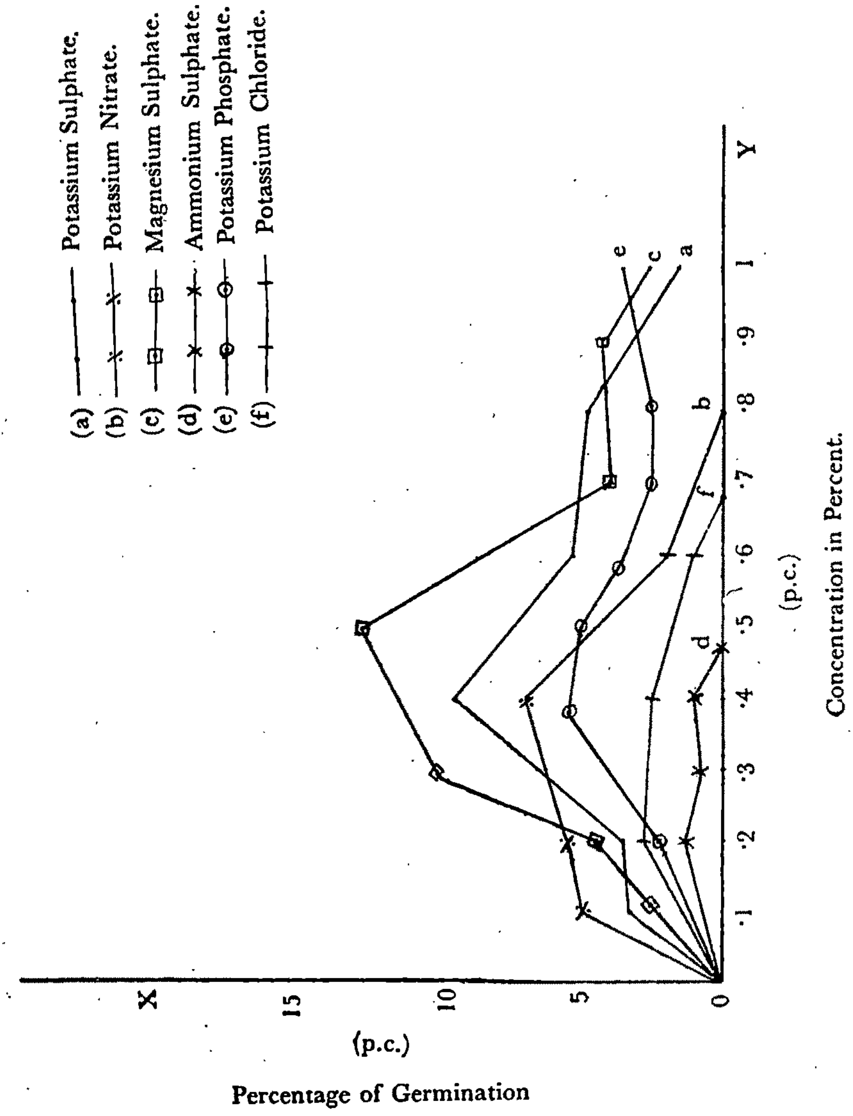
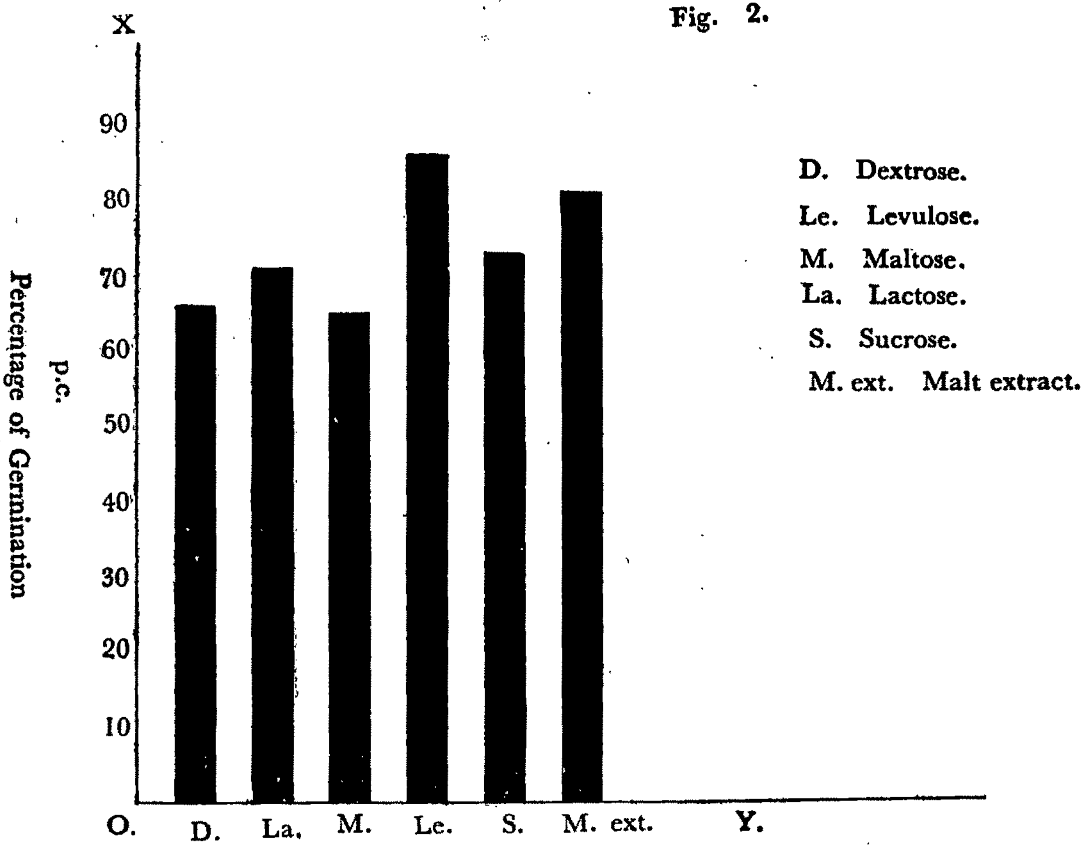

(a) Potassium Sulphate.
(b) Potassium Nitrate.
(c) Magnesium Sulphate.
(d) Ammonium Sulphate.
(e) Potassium Phosphate.
(f) Potassium Chloride.
X
15
10
5
0
(p.c.)
Percentage of Germination
·1
·2
·3
·4
·5
·6
·7
·8
·9
1
Y
(p.c.)
Concentration in Percent.
a
b
c
d
e
f

Fig. 2.


X
90
80
70
60
50
40
30
20
10
O.
D.
La.
M.
Le.
S.
M. ext.
Y.
p.c.
Percentage of Germination
D. Dextrose.
Le. Levulose.
M. Maltose.
La. Lactose.
S. Sucrose.
M. ext. Malt extract.

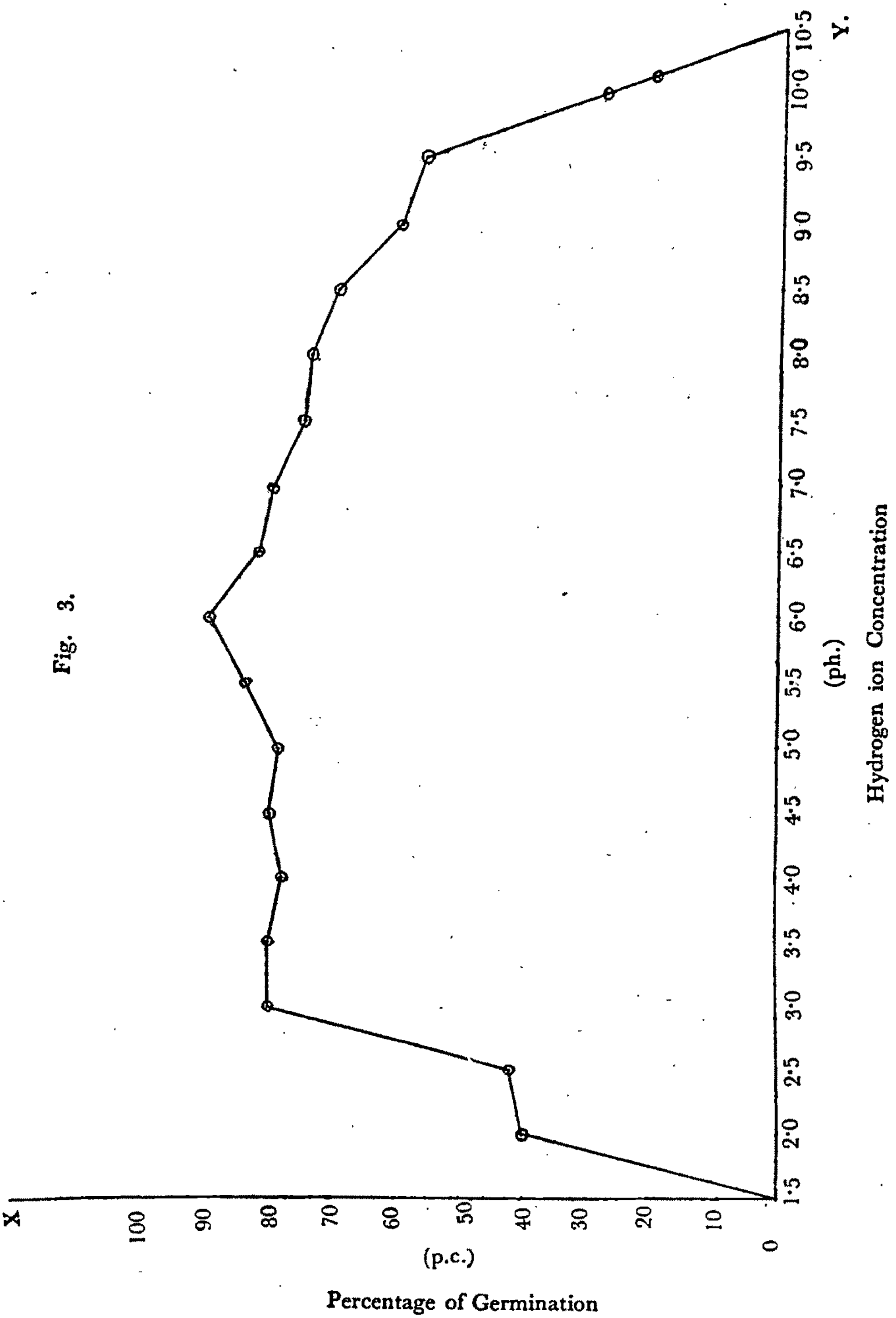


Fig. 3.

X
100
90
80
70
60
50
40
30
20
10
0
(p.c.)
Percentage of Germination
Y.
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
6·0
6·5
7·0
7·5
8·0
8·5
9·0
9·5
10·0
10·5
(ph.)
Hydrogen ion Concentration

AN ATTEMPT AT THE PREPARATION OF SILICON NITRITE

By P. D. GOYAL, R. L. SAKSENA, and P. S. SAKSENA,
Chemical Laboratories, Agra College, Agra

INTRODUCTION

It is well known that although carbon and silicon are the first and second members of the 4th group of the periodic classification, there is considerable difference in the properties of some of their compounds. The most obvious is the difference between CO_2 and SiO_2, the former being a gas while the latter is a high melting solid. According to G. N. Lewis CO_2 is normal whereas SiO_2 is polymerised in which the unshared electrons help the process of polymerisation.

There is a similar contrast in properties between the chlorides of the two elements. CCl_4 behaves abnormally and is not an acid chloride as would otherwise be expected, because it does not react with water or even dilute alkalis, but $SiCl_4$ hydrolyses in contact with water and forms $Si(OH)_4$. In fact CCl_4 behaves as one of the most inert compounds in organic chemistry. The reason for this difference in their behaviours can be explained on the basis of the electronic theory. The chloride atoms in CCl_4 are linked with covalent bonds to carbon atoms but in the case of $SiCl_4$, the chlorine atoms can be regarded as radicals of hydrochloric acid. Efforts have been made in the past to replace the Cl atoms in $SiCl_4$. Thus Reynolds prepared silicon thiocyanate from silicon tetrachloride and Lead thio cyanate (J. C. S., 89, 397, 1906).

$$SiCl_4+2\ Pb(SCN)_2=Si(SCN)_4+2\ PbCl_2$$

Forbes and Andrews (J. A. C. S. 62, 761, 1940) while attempting the action of silver (Iso) cyanate on $SiCl_4$ in benzene obtained two isomeric silicon cyanates.

$$Si\ Cl_4+4Ag\ O\cdot CN=Ag\ Cl+Si\ (OCN)_4$$

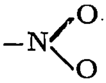
These isomeric compounds differ from one another in their boiling points and melting points. To these compounds the authors have assigned the cyanate and isocyanate struchers.

$Si(OCN)_4$	$Si\ (NCO)_4$
Cyanate	Isocyanate

As cyanic or thiocyanic acids can be regarded both as organic or inorganic acids, it was proposed to attempt to combine the silicon with a purely inorganic acid radical and the nitrous acid radical O – N — O was chosen for the purpose for the following reasons.

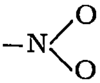
(1) The nitrous acid radical allows the possibility of isomerism as in the case of cyanic acid.

$-O-C\equiv N$ $-N=C=O$
Cyanate Isocyanate
$-O-N=O$
Nitrite



$-N\langle{}^{O}_{O}$

Nitro compound

(2) Tetranitro methane $C(No_2)_4$ has recently received much attention in organic chemistry. It is the most delicates tost for the presence of double bonds. It can be prepared with difficulty and only indirectly as the Cl atoms in Ccl_4 are so stable that they cannot be displaced by nitro groups coming, say from silver nitrite. As Cl atoms in $SiCl_4$ are active, it was thought that it may be possible to replace them by nitrous acid radical $-O-N=O$ from sodium nitrite or by nitro group  $-N\langle{}^{O}_{O}$ coming from silvernitrite. It tetra nitro-silane could be formed it would certainly be most interesting and useful compound.

EXPERIMENTAL

A. *Reaction between Silver nitrite and Silicon Tetrachloride*

The reaction chosen was similar to that chosen by Forbes aud Andrews (loc. cit.) and was carried out as follows.

$Sicl_4$ (2·7 cc.) dissolved in dry ether was added to a suspension of Ag No_2 (15 grms.) in the same medium. A cork carrying each tube was pu at the mouth of the flask. Heat was evolved and it was necessary to cool the reaction mixture from outside with ice water. The reaction was expected to proceed as follows.

$Sicl_4+4\ Ag\ No_2=4\ Ag\ cl+Si\ (No_2)_4$

The progress of the reaction was watched by formation of some brown vapours in the reaction vessel and by the development of a bluish colour in the solid. This might be due to the effect of light on Agcl formed in the reaction. From the filtrate the solvent ether (B. P. 34° C) and the unchanged $SiCl_4$ (B. P. 57.5°C) were removed by cautious distillation on a water bath. Last traces of ether and Si Cl_4 were removed by raising the temperature of the water bath to 70°C and applying suction.

The viscous mass left after distillation when heated with CaF_2 and H_2SO_4 gave SiF_4. The solid residue that remained behind was found to contain the unreacted Ag No_2, AgCl and in addition silicon also. This proved that during the course of the reaction two silicon compounds are formed ; one of which is soluble in ether and the other insoluble in it and remains mixed with $AgNo_2$ and Ag Cl.

Efforts to separate this second compound were unsuccessful as it was hydrolysed by water and was insoluble in common organic solvents. The method of Soxehelot was also tried to isolate it but it gave negative results.

Attempts to distil the viscous solid were unsuccessful as it began to decompose with evolution of brown vapours. The crude liquid was therefore analysed and found to be practically free from chlorine.

The silicon in the compound was estimated by adding A. R. caustic potash to a known weight of compound and evaporating the solution on water bath. Dilute $H.NO._3$ was then added and the mixture again evaporated. The residue was treated with water which dissolved soluble salts leaving behind a fine precipitate of silica, which was washed, dried and weighed.

For quantitative estimation of (-O- N=O) group a known weight of the compound (·1 to ·2 gm.) was treated with aqueous kosh and gently warmed. A definite volume of acidified $KMnO_4$ (in excess) was added and the contents were allowed to stand for some time at 40°C to ensure complete oxidation of nitrite to nitrate group. The remaining $KMnO_4$ was found by titrating against standard oxalic acid.

The results of the quantitative estimations for the viscous mass are as follows :

Si—7.3%, O—N=O 60%

As there is no chlorine in the compound, it can be safely concluded that the compound is not pure and therefore no conclusion can be drawn about the composition from the analytical data.

B. *The Reaction beetween Nitrogen peroxide and* $SiCl_4$:—When $SiCl_4$ was gradually added to liquid Nitrogen peroxide obtained from leadnitrate and liquefied in a freezing mixture, there was an appreciable increase in volume, the reacting liquids first turning green and ultimately deep red. The reaction was carried out below O°C. After some time a small amount of crystalline solid began to separate. After all $SiCl_4$ was added to the solution and the whole left overnight at O°C it was noticed that a small amount of a gas is evolved which liberates iodine from potassium iodide. The gas can be chlorine which is displaced from $SiCl_4$ or may be nitrogen peroxide (which also liberates I_2 from KI). It is however much less likely that No_2 was evolved as the temperature was below O°C at which temperature N_2O_4 or No_2 is a liquid

After standing overnight a good amouut of solid was deposited from the reaction mixture. Analysis of the Compound showed that it contained, silicon chlorine and nitrite radicals.

The compound was found to possess the following properties:—

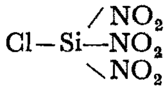
It is a strong reducing agent. It decolorised acidified permanganate in cold. When it is mixed with powdered $K_2Cr_20_7$ and then acidified with strong H_2 $S0_4$ the dichromate is at once reduced to green chromic sulphate. When heated with H_2SO_4 alone it turns the acid deep brown due obviously to nitrous fumes. It dissolves in hot koh solution from which silicic acid is formed on acidification.

The compound was found to give quantitative results for the nitrous acid radical which is in combination with silicon, and as such there is no possibility of the presence of the nitro group in the compound. Nitro group is estimated by treating the substance with $SnCl_2$ which reduces No_2 to NH_2 group. The treatment of this new silicon compound with $SnCl_2$ gave negative results.

The percentage of various elements found in the compound is as follows:—

Si	16·99
Cl	20·50
No_2	62·20

On the basis of these results the following formula is suggested for this new compound.



$$Cl-Si\begin{matrix}/NO_2\\-NO_2\\\backslash NO_2\end{matrix}$$

Reaction between $SiCl_4$ and $NaNO_2$

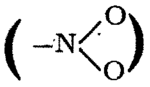
14 gms dry $NaNO_2$ was suspended in ether medium in a conical flask which was coled in freezing mixture and to this was added gradually a solution of 8 gms. of $SiCl_4$ in absolute ether. The reaction was more vigorous than that between $AgNO_2$ and $SiCl_4$ and brown fumes of oxides of Nitrogen were evolved. The liquid in the flask turned blue due to oxides of Nitrogen. The flask was stoppered and left overnight, the colour of the ethereal layer turning yellow. The ethereal layer was decanted and then distilled. Ether was first removed on a water bath and then distilled under reduced pressure. In this case temperature could be raised up to 90^{o}c and a small portion of the substance could be distilled without decomposition. The distilled portion when puton ice solidified and remelted at ordinary temprature, while that remains in flask did not solidify at that temperature. This shows that porbably two compounds are formed which are isomeric.

Properties of distillate:—The distillate when heated with conc H_2SO_4 gave brown fumes of NO_2 on treatment with KOH and acidifying with acetic acid and adding KI, I_2 was liberated. To a small portion of the compound KOH was added and then acidified with HNO_3 and then $AgNO_3$ was added, a curdy white ppt. was obtained indicating the presence of Cl_2in the compound.

In this case also the solid mass that remained behind in the reaction vessel after decantation of the ethereal layer was shaken up with water in which the soluble $NaNo_2$ and NaCl were washed away and a small residue was left. When this was tested, it showed the presence of Si in it showing there by that here too, two substances are formed, one of which is soluble in ether and the other insoluble in it. We were not successful in separating this insoluble compound.

In the course of quantitative estimations done on the compound obtained on distillation from the ethereal layer it was found that it contained 22·4%

Si and 28%Cl. No estimation of NO_2 group could be carried out as no compound was left with us.

The compound obtained in this case is different than the one previously ubtained. This probably contains two atoms of Cl in association with Si and the two atoms have been replaced by $(-O-N=O)$ or  $\left(-N\begin{smallmatrix}O\\O\end{smallmatrix}\right)$ group. But no definite conclusion could be drawn as to the constitution or structure because of the minute quantities of impure substance obtained for which there is no suitable method of purification and crystallisation. Further the lack of a suitable solvent poses another grave problem.

Reaction between Amylnitrite and Si Cl_4

The main difficulty experienced in the attempts to prepare silicon compounds of desired composition is that two silicon compounds are formed of which the one soluble in organic solvents is in very small proportion while the other which is a solid insoluble in organic solvents is the main product of reaction. This main product cannot be separated from metallic chlorides or the nitrite nor can it be extracted with water as it will be hydrolysed. It was therefore thought that replacement of a metallic nitrite by an organic nitrite may be of value. An easily awailable and convenient organic nitrite is amylnitrite $C_5H_{11}ON=O$. It is a liquid which boils at about 96°c. The amyl chloride that would be formed from it if the reaction takes following course.

$4(C_5H_{11}\ ON=O)+SiCl_7=Si(ON=O)_4+4C_3H_{11}Cl$ is also a liquid.

This reaction was therefore tried. Amylnitrite and silicon tetra chloride were brought into contact in ether solution at O°C. The reaction was vigorous and gases were evolved which threw away the stopper of glass bottle in which the reaction was carried out. The mixture was allowed to remain for four days and then the excess of $SiCl_4$ and ether were removed on a water bath. A liquid was left behind which was fractionated and the following fractions were collected.

Fraction I boiling between	140°	and	150°c
... II	210°	...	220°c
... III	250°	...	270°c

Fraction I on account of its comparitively low boiling point is likely to contain unchanged amylnitrite. Fraction II was the main bulk, and its boiling point varied within a small range of 10°. Fraction III was in smaller quantities and its boiling point varied in a wider range. From the point of purity fraction II is therefore better.

On examination it was found that each of these three fractions contained silicon but the surprising thing about them is that they also contain carbon. These therefore contain an organo-inorganic compound as they contain both carbon and silicon. All these fractions contain chlorine also. The presence of nitrogen in them was established by carrying out the usual test for nitrogen in organic compounds. The following results were obtained on analysis of fraction II.

Si 8.7% Cl 10.7%.

The nitrite group could not be estimated.

CONCLUSION.

(i) The action of silicon tetra chloride on a metallic nitrite results in the formation of two silicon compounds, the one which is in considerable preponderance is a solid insoluble in organic solvents and hydrolysable by water. The other which is formed only in small amount is a liquid except in the case of reaction between N_2O_4 and $SiCl_4$, soluble in organic solvents and not easily hydrolysable.

(ii) When the reaction was carried out with silver nitrite the liquid silicon compound contained silicon and $O-N=O$ group and was practically free from chlorine.

(iii) When the reaction was carried out with liquid nitrogen peroxide, Si, Cl and NO_2 groups, the probable formula for the compound is $Cl-Si-(NO_2)_3$

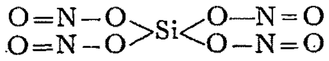
(iv) When the reaction was carried out with sodium nitrite, the liquid silicon compound contained chlorine. Two definitely different products have been obtained, one solidifies on cooling the other does not. But on account of uncertainty about their purity, no definite inference can be drawn about their composition.

(v) When an organic nitrite such as amyl nitrite $C_5H_{11}ON=O$ is treated with $SiCl_4$ a liquid silicon, compound is formed which contains silicon, chlorine and nitrogen. It also contains in addition carbon. Due to complexity about its composition its complete analysis was not achieved.

On the basis of the qualitative tests and available analytical data the following formulae for the compounds obtained can be predicted.

(I) Reaction with Silver nitrite :—

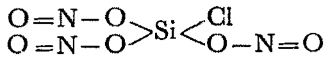
(Si 7.33%, $O-N=O-60\%$)



$$\begin{matrix} O{=}N{-}O \\ O{=}N{-}O \end{matrix} > Si < \begin{matrix} O{-}N{=}O \\ O{-}N{=}O \end{matrix}$$

(II) Reaction with liquid Nitrogen peroxide :—

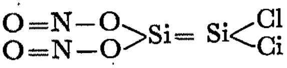
(Si 16.99%, cl 20.5%, $N_2-62.2\%$).



$$\begin{matrix} O{=}N{-}O \\ O{=}N{-}O \end{matrix} > Si < \begin{matrix} Cl \\ O{-}N{=}O \end{matrix}$$

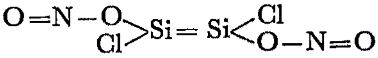
(III) Reaction between $\mathrm{NaNo_2}$ and $\mathrm{SiCl_4}$

(Si–22.4%, Cl–28%.)



$$\left.\begin{matrix}\mathrm{O{=}N{-}O}\\\mathrm{O{=}N{-}O}\end{matrix}\right>\mathrm{Si{=}\ Si}\left<\begin{matrix}\mathrm{Cl}\\\mathrm{Ci}\end{matrix}\right.$$

Or

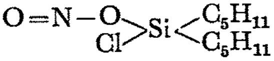


$$\left.\begin{matrix}\mathrm{O{=}N{-}O}\\\mathrm{Cl}\end{matrix}\right>\mathrm{Si{=}\ Si}\left<\begin{matrix}\mathrm{Cl}\\\mathrm{O{-}N{=}O}\end{matrix}\right.$$

(IV) Reaction with amyl nitrite

(Si–11%, Cl–16.24%.)

The problable formula, keeping in view the above pereentage figures and carbon and nitrogen Content is as follows:—



$$\left.\begin{matrix}\mathrm{O{=}N{-}O}\\\mathrm{Cl}\end{matrix}\right>\mathrm{Si}\left<\begin{matrix}\mathrm{C_5H_{11}}\\\mathrm{C_5H_{11}}\end{matrix}\right.$$

(Di amyl mono nitro Oil one)

A CRITICAL SURVEY OF VARIOUS METHODS OF DETERMINING COPPER VOLUMETRICALLY BY 'IODIDE-THIOCYANATE' METHOD USING SODIUM IODIDE IN PLACE OF POTASSIUM IODIDE.

By P. D. Goyal and S. D. Bhatia, *Agra College, Agra.*

E. D. Haens' volumetric iodine process for the estimation of copper is based on the fact that when an excess of Potassium iodide is added to the solution of a cupric salt, cuprous iodide is formed with an equivalent amount of free iodine the latter being estimated by titration against standard Sodium thiosulphate solution. Starch is added as an indicator towards end of reaction. If the cupric salt solution is very dilute the cuprous iodide produced in the reaction re-forms the original salt. This causes the phenomena of "after blueing". To prevent "after blueing" and to obtain a sharp end point potassium iodide has to be added in large excess (7 to 8 gms). The latter dissolves the precipitated cuprous iodide by forming with it a complex salt.

Potassium iodide being expensive G. Bruhns (chem. zeit. (1918), *42*, 301-302) zeit. Anal. chem. (1920). *59*; 337-359). suggested modification in the iodometric titration method by replacing part of potassium iodide by the cheap Ammonium or Potassium thiocyanate. The cuprous thiocyanate which is formed is less soluble than cuprous iodide. Bruhn used two alternative procedures for titration of a copper salt solution. In the first the copper salt solution in the presence of potassium iodide was titrated against a solution containing 24·8 gms of crystallised Sodium thiosulphate and 25-30 gms of Potassium thiocyanate per litre, starch being used as an indicator. In the second the copper salt solution was directly titrated against a solution containing 24·8 gms of crystnllised Sodium thiosulphate, 25 gms of potassium thiocyanate and 8gms of Potassium iodide per litre in the presence of starch.

W. Orlik and W. Tietze (chem. zeit.) (1930), *59* 174-175) in view of the high cost of carrying out the usual iodide method modified it by addition of thiocyanate to copper salt solution followed by addition of Potassium iodide and immediate titration against sodium thiosulphate.

Fowels recommended addition of potassium iodide followed by addition of thiocyanate and immediate titration against sodium thiosulphate, while Vogel used a mixture of excess of thiocyanate and a little potassium iodide with copper salt solution and titrated against standard sodium thiosulphate.

Foote and Vance (J. Amer. Chem. Soc. (1935), *57*, 845-847) found that the addition of a solution of potassium thiocyanate near the end point of the usual iodometric titration of copper increases the sharpness of the end point and accuracy of the method.. Out of the total amount of iodine liberated in reaction (1) a small amount is adsorbed on the surface of cuprous iodide molecules. If a thiocyanate solution is added the cuprous iodide formed in reaction (1) changes into cuprous thiocyanate reaction (3) and the adsorbed iodine becomes available for reaction against sodium thiosulphate-reaction (2)

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4 \ldots\ldots\ldots\ldots (1)$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6 \ldots\ldots\ldots\ldots (2)$$
$$Cu_2I_2 + 2KSCN = Cu_2(SCN)_2 + 2\,KI \ldots\ldots\ldots\ldots (3)$$

The total iodine measured by reaction (2) is closely equivalent to the copper, and the end point is sharp the precipitate turning almost white.

Another advantage of addition of potassium thiocyanate (reaction 3) is that the liberated potassium iodide becomes available again to react with more, cupric salt (reaction 1). The process thus repeats and all the cupric salt becomes cuprous thiocyanate with liberation of equivalent amount of iodine.

If potassium thiocyanate is added to copper salt solution prior to the addition of potassium iodide the cupric thiocyanate formed in reaction (4) slowly decomposes producing cuprous thiocyanate and sulphur as precipitates (reaction 5).

$$CuSO_4 + + 2KSCN = Cu(SCN)_2 + K_2SO_4 \ldots\ldots\ldots\ldots (4)$$
$$2Cu(SCN)_2 = Cu_2(SCN)_2 + (CN)_2 + 2S \ldots\ldots\ldots\ldots (5)$$

Thus the result is withdrawl of copper from solution with a consequent decrease in the amount of iodine liberated in reaction (1).

It is clear therefore that although potassium or ammonium this cyanate may replace part of the expensive potassium iodide, the mode of addition of thiocyanate has an important bearing on the accuracy of this determination and unless it is added when most of the cupric salt has been converted into cuprous salt, it may interfere with the accuracy of the method.

From the various methods that have been considered above it appears that although there is a general agreement regarding Bruhn's original suggestion about addition of thiocyanate in the iodometric determination of copper opinions differ as to the mode of addition.

The method of Foote and Vance appears to be capable of giving accurate results. It was therefore studied in details.

The present investigation was undertaken with a view (1) to see how far Bruhn's idea of replacing part of the expensive potassium iodide by the cheaper thiocyanate is compatible with accuracy of copper estimation and to ascertain the merits of the various procedures in carrying out the iodometric titrations. (2) to see whether sodium iodide could replace the expensive potassium iodide.

EXPERIMENTAL

The apparatus used was calibrated in the usual manner. The solutions of copper sulphate employed were 0.5, 0.2, 0.1, 0.0625, 0.05 and 0.02 Normal.

Solutions of sodium thiosulphate used were of corresponding strengths. Potassium iodide, or sodium iodide and ammonium thiocyanate were employed in 10 percent strength. When larger amounts were needed the salts were used as solids. The investigations were done in the following series.

Series 1:— No thiocyanate was used. The effect of addition of potassium or sodium iodide in decreasing amounts to copper salt solution on the correctness of copper estimation was observed. It was found that

(a) the use of sodium iodide in place of potassium iodide causes no change in estimation.

(b) the estimated value of copper becomes less than the actual value when amount of potassium or sodium iodide added goes belong a certain limit, althought this amount is still higher than what is required to react with the copper salt as in equation (1). For instance for 10 c.c. of 0.1N copper salt solution the minimum amount of potassium iodide to be added to get a correct value is 2 gms.

Series 2:—Estimations carried out with solutions as suggested by Bruhns (para 2 page 1) failed to give correct results.

Procedure (1), (Ref. Page 1, para 2)

Table I

Titration of a solution of copper sulphate containing 124.2257 gms. of the hydrated salt (A. R.) per litre against a mixture containing 2.5 gms. of ammonium thiocyanate made to 250 c.c. with. 5 N sodium thiosulphate, using varying amounts of 10% potassium iodide solution.

Copper sulphate taken	Potassium iodide (10%) added.	Thiosulphate used	Percentage cf copper
10 cc.	20 cc.	10.2 cc,	102.5
,,	15 cc.	10.15 cc.	102.0
,,	10 cc.	10.15 cc.	102.0
,,	8 cc.	10.15 cc.	102.0
,,	6 cc.	10.15 cc.	102.0
,,	4 cc.	10.1 cc.	101.5
,,	2 ce.	10.05 cc.	101.05
,,	1 cc.	10.0 cc.	100.5
,,	.5 cc.	9.9 cc.	99.49

Similar inconsistent results were obtained when sodium iodide was used instead of potassium iodide in the above experiments.

Procedure (2) (Ref. Page 1, para 2).

Table II

Titration of copper sulphate solution containing 49.6903 gms. of hydrated salt (A. R.) per litre against a mixture of .2N sodium thiosulphate plus 20% potassium iodide plus 10% ammonium thio cyanate.

Copper sulphate taken	Thiosulphate used	Percentage of copper
10 cc.	10.95 cc.	110.05
10 cc.	10.9 cc.	109.5
10 cc.	10.95 cc.	110.05

These experiments show that by the use of the mixed solutions the thiosulphate is partially oxidised, so that the results obtained are high. By increasing the concentration of potassium iodide or by using sodium iodide in place of potassium iodide the results were found to be unaffected.

Series 3:—The method of Orlik and Tietze, of adding to copper salt solution first ammonium thtocyanate and then potassium or sodium iodide was examined. The estimated values were inconsistent and low as would be evident from the results of experiments tabulated below (Table III).

It was also observed that:—

(a) Increase in the ratio of ammonium thiocyanate, potassium or sodium iodide lowered the estimated value while a dicrease in the ratio improved them.

(b) The larger the time interval between the addition of ammonium thiocyanate and that of potassium or sodium iodide the lower was the estimated value.

Table III

Titration of a solution of copper sulphate containing 123.6015 gms of the hydrated salt (A. R.) per litre against 0.5 N sodium thiosulphate using varying amounts of ammonium thiocyanate (10%) followed by potassium iodide (10%).

Copper sulphate taken	Potassium iodide added	Thiocyanate added	Thiosulphate used	Percentage of copper.
10 cc.	10 cc.	10 cc.	9.45 cc.	95.49
10 cc.	10 cc.	10 cc.	9.4 cc.	94.9
10 cc.	10 cc.	20 cc.	9.3 cc.	93.9
10 cc.	10 cc.	20 cc.	8.9 cc.	89.9
10 cc.	5 cc.	20 cc.	9.1 cc.	91.9
10 cc.	5 cc.	20 cc.	8.95 cc.	90.49
10 cc.	5 cc.	5 cc.	9.5 cc.	95.9
10 cc.	5 cc.	5 cc.	9.45 cc.	95.49
10 cc.	4 cc.	2 cc.	9.7 cc.	97.9
10 cc.	4 cc.	2 cc.	9.8 cc.	98.9
10 cc.	20 cc.	20 cc.	9.5 cc.	95.9
10 cc.	20 cc.	20 cc.	9.1 cc.	91.9
10 cc.	Excess of iodide only		9.9 cc.	100.0

Series 4:—The method of Fowels of addition of potassium or sodium iodide to copper salt solution followed by addition of ammonium thiocyanate was tested. The estimated values were better although lower than the actual values. Increase in the amount of iodide makes the values still better. All these points will be clear from the results of one of such experiments tabulated below in Table No. IV.

Table IV

Titration of a solution of copper sulphate containing 24.5363 gms. of the hydrated salt (A.R.) per litre against .09925 N sodium thiosulphate using varying amounts of 10% potassium iodide followed by 10% ammonium thiocyanate.

Copper sulphate taken	Potassium iodide added	Thiocyanate added	Thiosulphate used	Percentage of copper
10 cc.	10 cc.	20 cc.	9.8 cc.	99.5
10 cc.	5 cc.	20 cc.	9.8 cc.	98.98
10 cc.	5 cc.	20 cc.	9.85 cc.	99.5
10 cc.	2 cc.	20 cc.	9.8 cc.	98.98
10 cc.	2 cc.	20 cc.	9.75 cc.	98.4
10 cc.	2 cc.	10 cc.	9.8 cc.	98.98
10 cc.	2 cc.	10 cc.	9.7 cc.	97.9
10 cc.	2 cc.	2 cc.	9.6 cc.	96.9
10 cc.	1 cc.	20 cc.	9.3 cc.	93.9
10 cc.	Excess of iodide only		9.9 cc.	100

In this case the end point is not easy to detect as the precipitate has a brownish colour. Dilution makes the detection of end point still difficult.

Series 5:—The method of Vogel of addition to the copper salt solution of a mixture of thiocyanate and iodide was examined. The results were not satisfactory and the method was found to suffer from the same defects as mentioned in series 3 and 4. Results of a typical experiment are tabulated in Table No. V.

Table V

Titration of a solution of copper sulphate containing 24.5363 gms. of the salt (A. R.) per litre against .09925 N sodium thiosulphate with the addition of 25 cc. of a mixture of potassium thsocyanate and potassium iodide (containing quantities given below.)

Coper sulphate taken	Potassium iodide in mixture	Thiocyanate in the mixture	Thiosulphate used	Copper percentage
10 cc	.1 gm.	2 gms	8.8 cc	98.0
10 cc	.2 gm	2 gms	8.9 cc	90.0
10 cc	.3 gm	2 gms	8.95 cc	90.47
10 cc	.4 gm	2 gms	9.1 cc	91.9
10 cc	.5 gm	2 gms	9.3 cc	93.93
10 cc	.6 gm	2 gms	9.55 cc	96.4
10 cc	.7 gm	2 gms	9.7 cc	98.0
10 cc	.8 gm	2 gms	9.75 cc	98.5
10 cc	.9 gm	2 gms	9.8 cc	98.98
10 cc	1.0 gm	2 gms	9.85 cc	99.5
10 cc	Excess of iodide only.		9.9 cc	100.0.

Series 6:—In this series the method of Foote and Vance was tried with solutions of different concentrations. Following the details of the method given by Voge and Rieman and Neuss the following procedure was adopted.

To 10 cc. of copper sulphate solution (containing a known weight of the hydrated A. R. salt) contained in a 250 cc. conical flask was added 10% solution of sodium or potassium iodide (volumes of the iodide solution added are shown in the tables); and the mixture titrated against standard sodium thiosulphate solution, until the yellow colour due to liberated iodine becomes faint, 2 cc. of freshly prepared starch solution is then added and the titration continued until the blue colour becomes faint About 15 cc. of a 10% solution of ammonium thiocyanate is now added (which liberates the iodine adsorbed on the cuprous iodide causing deepening of blue colour) and titration continued until the blue colour just disappears. The results of some of such experiments are shown below in the table VI.

Table VI

Titration of copper sulphate solution containing 124.2257 gms. of the salt (A. R.) per litre against 0.5 N sodium thiosulphate solution using ammonium thiocyanate and decreasing quantities of potassium iodide (10% solution).

Copper sulphate taken	Potassium iodide added	Thiocyanate added	Thiosulphate used	Percentage of copper
10 cc	20 cc	20 cc	9.95 cc	100
10 cc	18 cc	20 cc	9.95 cc	100
10 cc	16 cc	20 cc	9.95 cc	100
10 cc	14 cc	20 cc	9.95 cc	100
10 cc	12 cc	20 cc	9.95 cc	100
10 cc	10 cc	20 cc	9.95 cc	100
10 cc	9 cc	20 cc	9.95 cc	100
10 cc	8 cc	20 cc	9.95 cc	100
10 cc	7 cc	20 cc	9.95 cc	100
10 cc	6 cc	20 cc	9.95 cc	100
10 cc	5 cc	20 cc	9.95 cc	100
10 cc	4 cc	20 cc	9.90 cc	99.5
10 cc	3 cc	20 cc	9.8 cc	98.4
10 cc	3 cc	20 cc	9.7 cc	97.48
10 cc	2 cc	20 cc	9.3 cc	93.46
10 cc	2 cc	20 cc	9.1 cc	91.45
10 cc	2 cc	20 cc	9.2 cc	92.46
10 cc	1 cc	20 cc	9.1 cc	91.4
10 cc	1 cc	20 cc	9.05 cc	90.9

CONCLUSIONS

From the results tabulated above it is clear that:

1. Ammonium or potassium thiocyanate can replace part of the expensive potassium iodide in the iodometric determination of copper in cupric salt solutions.
2. The use of mixed solutions of iodide and thiocyanate gives inaccurate results.
3. The addition of thiocyanate just before the end point is reached (i. e. when the blue colour due to starch and iodine begins to fade) gives accurate and reproducible results. The end point is sharp and easy to detect as the colour of the precipitate is almost white. The method gives stoichiometric results. Only few c.c.s of the thiocyanate solution are required for completion of reaction.
4. For a solution of cupric salt containing about 0.06 gms. of copper only about 0.2 gms. of potasslum or sodium iodide will be sufficient.
5. Since the actions of sodium iodide and potassium iodide are identical the former can conveniently and profitably be substituted for the latter.

The saving in .the cost of iodide can be appreciated by reviewing the amount of potassium iodide recommended in standard works on analytical chemistry. Thus cumming and Kay, Basset, clowes and coleman, Treadwell and Hall, Sutton, and Millor add about 3 gms. of potassium iodide for 0.2 to 0.25 gms. of copper. Finally Vogel, Riemann and Neuss adopting Foote and Vance method recommend addition of 3 gms. of potassium iodide dissolved in 10 cc. of water for 0.2 gms. of copper.

CHANGES IN THE TOTAL CATION EXCHANGE CAPACITY IN THE DUMAT SOIL OF AGRA DISTRICT BY HUMIFYING THE LEGUMINOUS WEEDS—(i) WILD INDIGO (TEPHROSIA PURPUREA) AND (2) JWASA ALHAGI CAMELORUM).

By B. R. Nagar and Abani K. Bhattacharya, *Professor of Chemistry, Agra College, Agra.*

Parker and Pate (1926) observed a good relation between $\frac{SiO_2}{R_2O_3}$ ratio of soil colloids, and the total exchangeable bases, while Williams (1932), Mc. George (1934), Smolik (1933), Miller and Co-workers (1936), and Baver (1930) observed that the base exchange phenomenon was a very complicated function of the clay fraction as well as of the organic matter of the soil. The PH of the soil was no less important in determining the base exchange capacity of the soil. Deramonova and co-workers (1940) observed that the base exchange capacity was increased ten fold with the the change of PH from 2-13, and they found a linear relationship between them.

In view of the complications involved in the base exchange phenomenon it was deemed necessary to make a critical study of the role of $\frac{SiO_2}{R_2O_3}$ ratio. residual organic matter in the soil, and PH values in determining the total cation exchange capacity of the soil complex. In this paper the results of our study on the total exchangeable cations vis-avis the $\frac{SiO_2}{R_2O_3}$ ratios, residual organic matter in the soil after humification of weeds, and PH have been given and discussed.

Experimental

The adhering soil was removed from the weeds and they were pulverised, and sieved through 100 mesh sieve. The raw organic matter was mixed with the soil in the ratio of 20 parts of soil to 1 part by weight of the pulverised weed, and the whole quantity was macerated with distilled water and left under the shade to humify. The moisture content of the soil was maintained at 15% level by weighing on alternate days and adding the required amount of distilled water. At the end of 16 weeks soil samples were taken out and air dried. The soil samples thus obtained were properly sieved (100 mesh). The average of the four replicates is given in the table. Inorganic constituents of the weeds were estimated by the methods suggested by A.O.A.C.(1945). Total cation exchange capacity was determined by the method suggested by Piper (1947). Organic carbon was determined by Walkley's (1935) rapid titration method.

Table No. I

Analysis of soil and organics added for humification.

	Soil Sample	Wild Indigo (Tephrosia purpurea)	Jwasa (Alhagi camelorum)
Loss on ignition	3.803%	89.67%	90.44%
Sand	84.21%	2.82%	1.18%
Alkali soluble silica	-	2.25%	1.75%
Fe_2O_3	2.764%	0.008%	-
CaO	1.933%	2.37%	1.903%
MgO	0.1241%	0.351%	1.389%
Al_2O_3	6.206%	0.335%	0.497%
K_2O	0.453%	1.042%	1.619%
P_2O_5	0.1992%	0.589%	0.149%
SiO_2/R_2O_3 Ratio	-	25.33%	10.02%
*aTotal Sio_2			

Table No. II

Chqnges in total cation exchange capacity in the 'Dumat' soil of Agra district by humifying the leguminous weeds : (1) *Wild Indigo* (*Te phrosia purpurea*) *and* (2) *Jwasa* (*Alhagi camelorum*)

Soil Sample	Total cation Exchange	Organic carbon %	pH	$\frac{SiO_2}{R_2O_3}$ ratio of the weed
Untreated soil	7.5 m.e.	0.251%	7.80	-
Humified with leguminous *Wild Indigo* (Tephrosia-purpurea)	14.1 m.e.	1.050%	8.08	25.33
Humified with leguminous *Jwasa* (Alhagi-camelorum)	14.3am.e.	1.316%	8.08%	10.02

Reference to tabel No. 2 will show that there is 100% increase in the total cation exchange capacity of the soil by the humification of the two leguminous weeds, Wild Indigo (Tephrosia Purpurea) and Jwasa (Alhagi Camelorum). Our observation in this respect is similar to those of Smolik, Mc.George, Miller and co-workers and others. It is further suggested by our data that the changes in the total cation exchange capacity bear no correspondence to the $\frac{Si\,O_2}{R_2O_3}$ ratio of the weeds or the residual organic carbon taken as single factors. Our results, therefore, lead to the conclusion that the cation exchange capacity ultimately depends on the relative preponderance of the physico-chemical properties of the clay fractions and of clay minerals over those of the organic contents and vice versa. The PH values, however, show that the cation exchange capacity increases with rise in PH as had been observed by Deramonova, but the relative change in the exchange capacity with PH seems to be specific with the nature of the organic matter humified in the soil

SUMMARY

Changes in total exchange capacity were estimated in the soil of Agra District by humifying two indigenous leguminous weeds, Jwasa and Wild Indigo.

From our experimental observations it has been fairly concluded that (1) the cation exchange capacity depends upon the relative preponderance of the physico-chemical properties of clay fractions and of clayminerals over those of the organic contents of the soil and vice versa and (2) that the cation exchange capacity increases with the rise of the PH value of the system.

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INVESTIGATION OF THE KINETICS OF THE OXIDATION OF OXALIC ACID BY POTASSIUM PERSULPHATE

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ABSTRACT

The reaction between potassium persulphate and oxalic acid has been studied from the view point of kinetics. It has been found that the reaction progresses in two stages: (1) Auto-catalytic and (2) Normal, exhibiting a 'Zero-molecular' Order in normal course. Evidence has also been obtained that it is catalysed by glass surface and the overall reaction is governed by a heterogeneous cum homogeneous mechanism.

INTRODUCTION

The reaction between oxalic acid and potassium persulphate both, with and without a catalyst, has been studied by a number of workers. R. KEMPF[1] observed that the reaction without a catalyst is very slow at room temperature, while in the presence of a silver salt it is quite rapid as well as quantitative. KING and others,[2-6] studied the kinetics of the oxidation of oxalate, manganous, ammonium, chromium etc., ions by persulphate ion in the presence of $Ag^{\cdot}$ ion as catalyst and have suggested a mechanism for the catalysed reaction. SRIVASTAVA & GHOSH,[7] investigated the mechanism of the kinetics of this reaction, with and without a catalyst such as silver and copper ions. They observed that the reaction is auto-catalytic, and that neutral salts have a negative effect on the reaction. A period of induction has also been observed by them.

From the foregoing literature it may be seen that the kinetics of this reaction without a catalyst, studied so far, leaves enough room for it's further development with regard to the influence of surface, effect of salts, order of the reaction etc.

It was therefore deemed desirable to investigate this reaction from these aspects by studying its kinetics at higher temperatures. Our results of investigations are fairly reproducible and are being communicated in this paper.

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2. C. V. King. (J.A.C.S. 50, 2089, 1928).
3. D.M. Yost. (J.A.C.S. 48, 152-164, 1926).
4. C. V. King. (J.A.C.S. 49, 2689, 1927).
5. A.O.Dekker, H. A. Levy and D.M. Yost. (J.A.C.S. 59, 2129, 1937).
6. T.L.Allen. (J.A.C.S. 73, 3589, 1951).
7. Srivastava & Ghosh. (Zeitschr· fur Physikalische Chemie, 202, 191-197, 1953).

EXPERIMENTAL

Standard solutions of potassium persulphate (Kahlbaum A.G.) and oxalic acid (A.R.B.D.H.) were prepared in conductivity water. Their strengths were tested before use. Required amounts of potassium persulphate and oxalic acid solutions were taken in separate conical flasks and kept in the thermostat maintained at the temperature of the experiment. The reaction was started by mixing the two solutions in the reaction vessel. After suitable intervals of time 10 cc. of the reaction mixture was withdrawn and added to ice-cold water containing 5 cc. of 0.1 M. $MnSO_4$ solution and 5 cc of 4N. H_2SO_4. This was titrated with standard potassium permanganate solution in cold, thus estimating the amount of oxalic acid.

In order to estimate the amount of potassium persulphate, at various intervals, in the reaction mixture, a slight modification of Bartlott & Cotmann's[8] method was adopted. This consisted in adding 10 cc. of the reaction mixture to a solution consisting of 5 cc. of 40% KI, 5 cc. of 4% $NaHCO_3$ and 1 cc. of N. H_2SO_4 and titrating against standard Sodium thio-sulphate solution. The Zero and Uni-molecular velocity coefficients were calculated by the usual formulae: $K_0=x/t$; and $K_1=2.303/t \log a/a\text{-}x$.

DETERMINATION OF THE ORDER OF THE REACTION:

The velocity coefficients of the reaction between potassium persulphate and oxalic acid were determined at 60° C and it's Order calculated by Ostwald's Isolation method. The results are summarized below:—

Table I

$K_2S_2O_8$=0.005 M; Oxalic Acid=0.1 M; Temp.=60° C.

t	(a-x)	K_0	K_1
0 mins.	18.5 c.c.	-	-
60	17.7	0.01333	0.0007369
120	16.9	0.01333	0.0007543
180	16.0	0.01389	0.0008072
240	15.3	0.01333	0.0007918
300	14.4	0.01366	0.0008352
360	13.5	0.01389	0.0008758
420	12.5	0.01429	0.0009340
480	11.6	0.01437	0.0009729
540	11.0	0.01389	0.0009629
600	10.3	0.01367	0.0009763
660	9.2	0.01409	0.0010590

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[8] Bartlott and Cotmann. (J·A.C.S. 71, 1419, 1949).

Table II

$K_2S_2O_8$=0.005 M; Oxalic Acid=0.125 M; Temp.=60° C.

t	(a-x)	K_0	K_1
0 mins.	18.5 c.c		
60	17.6	0.01500	0.0008330
120	16.8	0.01414	0.0008041
180	15.8	0.01500	0.0008764
240	14.9	0.01500	0.0009020
300	13.7	0.01600	0.0010020
360	12.4	0.01694	0.0011120
420	11.5	0.01666	0·0011320
480	10.7	0.01625	0.0011410
540	10.0	0.01574	.0011400
600	9.6	0.01484	.0010930
630	8.1	0.01651	0.0013120

Table III

$K_2S_2O_8$=0.05 M; Oxalic Acid=0.005 M; Temp.=60° C.

t	(a-x)	K_0	K_1
0 mins.	10.0	-	-
10	9.0	0.1000	0.01054
20	8.0	0.1000	0.01116
30	7·0	0.1000	0.01190
40	5.3	0.1177	0.01587
50	4.0	0.1200	0.01832
60	3.0	0.1166	0.02006
70	2.3	0.1100	0.02100
80	1.2	0·1100	0.02651
90	0.1	0.1100	0.05117

Table IV

$K_2S_2O_8$=0.02 M; Oxalic Acid=0.02 M; Temp. 60° C.

t	(a-x)	K_0	K_1
O mins.	5.2 cc.	-	-
60	4.8	0.00666	0.001336
120	4.4	0.00666	0.001391
180	4.2	0.00555	0.001187
240	3.9	0.00541	0.001199
300	3.8	0.00466	0.001046
360	3.6	0.00444	0.001022
420	3.3	0.00452	0.001083
480	3.1	0.00437	0·001077
540	2.9	0·00425	0.001081
600	2.8	0.00400	0.001031

Table V

$K_2S_2O_8$=0.02M; Oxalic Acid=0.02 M; Temp.=60° C.

t	(a-x)	K_0	K_1
0 mins.	8.1 cc.	-	-
60	7.5	0.01000	0.001278
120	6.8	0.01083	0.001458
180	6.4	0.00944	0·001309
240	6.1	0.00833	0.001182
300	5.6	0.00833	0.001230
360	5.2	0.00805	0.001231
420	4.7	0.00809	0.001296
480	4.2	0.00812	0.001369
540	3.8	0.00796	0.001402
600	3.4	0.00783	0.001446

From tables I and II it is observed that the values of K_1 continuously increase with the progress of the reaction. The velocity coefficient K_0 slightly increases in the beginning and then falls but remains fairly constant, indicating that the reaction is of 'Zero-Order' with respect to persulphate. Similarly from table III it is observed that the reaction is of zero-order with respect to oxalic acid. Thus the whole reaction should be of Zero Order. This conclusion is further supported by the values of K_0 (tables IV and V)., when the concentrations of the reactants are equal and the conditions of 'Isolation' method do not exist.

INFLUENCE OF TEMPERATURE

This reaction was further studied at various temperatures with a view to determine it's tentative temperature Coefficient and Activation Energy. The results are summarized below:—

Table VI

$K_2S_2O_8$=0.05M; Oxalic Acid=0.005 M; Temp.=55° C.

t	(a-x)	K_0	K_1
O mins.	10.0 c.c.	-	-
30	8.0	0.06666	0.007439
60	5.4	0.07666	0.010270
90	3.7	0.07000	0.011050
100	3.1	0.06900	0.011710
120	2.3	0.06420	0.012250
150	0.8	0.06130	0.016850
160	0.3	0.06060	0.021930

Table VII

$K_2S_2O_8$=0·05 M·; Oxalic Acid=0.005 M; Temp.=50° C.

t	(a-x)	K_0	K_1
0 mins.	10.0 c.c.	-	-
30	9.0	0.03333	0.003517
60	8.1	0.03166	0.003512
90	6.8	0.03555	0.004286
120	4.4	0.04666	0.006841
150	1.9	0.05400	0.011080
160	1.0	0.05625	0.014400
170	0.2	0.05760	0.023020

Table VIII

$K_2S_2O_8$=0.05M; Oxalic Acid=0·005 M; Temp.=45° C.

t	(a-x)	K_0	K_1
O mins.	10.0 c.c.	-	-
30	8.8	0.0400	0.004261
60	7.2	0.0466	0.005478
90	6.7	0·0366	0·004450
120	6.3	0.0308	0.003851
150	5.2	0.0320	0.004360
180	4.3	0.0317	0.004689

From the foregoing tables it is observed that the values of the velocity coefficient at 55° C., 50° C., and 45° C. also show slight increasing tendency in the beginning of the reaction and then decrease a little but remain fairly constant The temperature coefficient calculated from the value of Ko showing constancy at 50° C and 60° C; and 55° C and 45° C comes out to be 1.97 and the Activation Energy to be 13320-14070 cals.

INFLUENCE OF SURFACE

The reaction was studied by adding glass beads to the reaction mixture with a view to make variations in the surface/volume ratio. The results are summarized below:—

Table IX

$K_2S_2O_8$=0.05M; Oxalic Acid=0.005M; Temp.=60° C.

(a) With 100 Glass Beads:

t	(a-x)	K_0
O mins.	10.0 c.c.	-
20	7.6	0.1200
40	4.6	0.1350
60	1.2	0.1466
70	Reaction completed.	

(b) With 200 Glass Beads:

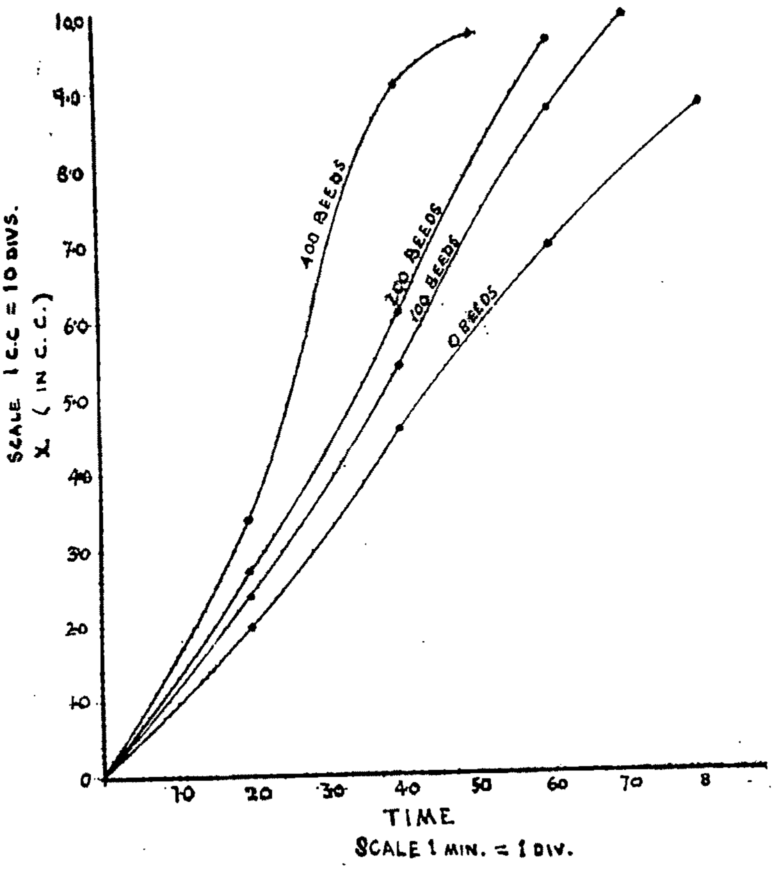
t	(a-x)	K_0
0 mins.	9.7 c.c.	-
20	7.3	0.1200
40	3.8	0.14735
60	Reaction Completed.	

(c) With 400 Glass Beads :

t	(a-x)	K_0
O mins.	9.7 c.c.	-
20	6.6	0.1500
40	0.9	0.2200
50	Reaction Completed.	

From the foregoing tables it is observedthat the values of the velocity coefficient K_0 do not show any appreciable constancy. Further it is interesting to note that the reaction comes to almost completion in 70 mins., with 100 glass beads; in 60 mins., with 200 glass beads; but in 40. mins., with 400 glass beads, while it takes 90 mins., for completion without beads. (vide table III.) It is evident therefore that the GLASS SURFACE plays an important role in catalysing this reaction. This suggests that the reaction may be partly heterogeneous being catalysed by glass surface. Further it is observed from the x-t curves (Fig. 1) that the amount of Oxalic acid decomposed at various intervals of time increases with the increase in the number of glass beads added to the reaction mixture

GRAPH BETWEEN 'x & t'



Influence of electrolytes

The decomposition of oxalic acid in presence of various electrolytes was studied in the usual manner and its results are summarized below:—

Table X.

TEMPERATURE=60° C.

$M=\frac{1}{2}\sum Ecz^2$	Electrolyte added	Fraction of Oxalic Acid Decomposed in 60 mins.
0.15	-	0.700
0.40	KCl	0.870
0·50	KCl	0.990
0.50	NaCl	0.750
0.50	CH_3COONa	0.180
0.60	$AlCl_3$	0.200
0.75	K_2SO_4	0.990
0.75	Na_2SO_4	0.880

From the foregoing tables it is observed that the neutral salts such as KCl, K_2SO_4, Na_2SO_4 have a positive influence on the velocity of the reaction, K ion being more active than Na· ion, while salts like $AlCl_3$ and CH_3COONa exert an inhibitive influence on it. The influence of these electrolytes depends upon the ionic strength as well as the nature of the ions. Increase of ionic strength of KCl, increases it's positive influence.

DISCUSSION

From the foregoing results it appears that the overall reaction progresses in two stages: (1) Auto-catalytic and (2) Normal. The auto-catalytic character is probably due to the chain mechanism of the reaction as suggested by T. L. Allen, or due to increase in activation of the reacting molecules on the surface of the glass of the reaction vessel, or both. The constancy in the values of K_0 in the later stages supports the heterogeneous character of the reaction as has been observed in the decomposition of Ammonia on molybdenum and tungsten, and in many other reactions catalysed by enzymes. This may be due to the reason that after some time the catalytic surface gets completely covered with the reactant molecules, so that the number of activated molecules remains constant. The slight decrease in the values of K_0 in the last stages is probably due to the reason that one of the reactants or products is strongly adsorbed with the result that it will prevent access of the other, or both the reactants to the glass surface; consequently the reaction gets retarded.

With the decrease of temperature, the activation of reacting molecules decreases and hence the velocity of the reaction also slows down. The activation energy (13320-14070 cals.) being much lower than the expected value for the zero-molecular reactions, supports our view that the reaction is catalysed by the glass surface of the reaction vessel either through 'chain mechanism or by surface activation, or both.' This is further confirmed by our observations on the influence of various electrolytes on the velocity of this reaction, which act as promoters or inhibitors in heterogeneous reactions.

In view of the foregoing results, the authors are of the opinion that the reaction is of Zonal character exhibiting zero-molecular order in it's later stages, and the overall reaction is governed by a homogenous cum heterogeneous mechanism. Further investigations on the reaction are in progress.

ACKNOWLEDGEMENT

The authors are greatly indebted to Dr. A. K. Bhattacharya, D.Sc., F.R.I.C., Head of the Chemistry Department, Agra College, Agra for his kind guidance in carrying out these investigations, without which it could not have been possible to bring out this publication.

THE STRENGTH OF HYDROGEN BOND AND PARACHOR

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INDRODUCTION

It is known that under certain conditions an atom of Hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond. It is largely ionic in character, and is formed only between the most electro-negative atoms. The strength of the bond increases with the increase in the electronegativity of the two bonded atoms. The strength of the hydrogen bond is determined by studying the bond energy or the absorption spectrum in the infra red region.

Bhagwat, Shukla and Khandekar (1) have investigated hydrogen bond formation from the study of Parachor. They have shown that when hydrogen bond is formed there is a sudden fall in the parachor value, of about ten units. They have studied the dimers of carboxylic acids in certain solvents. These carboxylic acids i.e. acetic acid, benzoic acid, propionic acid and butyric acid, form strong hydrogen bonds. Trivedi, Kaweeshwar and Bhagwat (2) have also studied the formation of hydrogen bond in p-cresyl methyl ether, when dissolved in alcohols, by parachor method.

Carboxilic acids, o-nitrophenol, methyl salicylate, salicylaldehyde form strong hydrogen bonds (3), while m-nitrophenol, p-nitrophenol, o-cresol, o-chlorophenol, resorcinol, hydroquinone and pyrogallol form weak hydrogen bonds (4). Our object is to examine whether or not the parachor values of these compounds in different solvents enable us to draw distinction between weak and strong hydrogen bonds. To arrive at a satisfactory conclusion a sufficiently large number of compounds have been dissolved in various solvents. A number of compounds forming weak hydrogen bonds, besides a few forming strong hydrogen bonds, have been examined, because already much work has been done on these latter.

EXPERIMENTAL

The measurement of Parachor involves determination of the surface tension and density of the substance in dissolved state. Density was determined by the usual type of pyknometer. The surface tension was determined by Jaegars method, which depends on the formation of bubble of air in the liquid. In the Jaegars method we have used a single capillary dipped up to a definite hight inside the solution under examination. A water aspirator and a manometer was used. The manometeric liquid was ethyl alcohol coloured with methyl blue.

In calculating the parachor of the solute in solution the mixture law of Hanmick and Andrew (5) has been used viz.

$Pm=P\ (1-x)+Px\ X$ and $Pm\frac{Mm\ \gamma^{\frac{1}{4}}}{D}$, where Mm is the mean molecular weight of the solution. The substances employed by us were of A. R. quality and of E. Merk or B. D. H. make.

Results

Our results which are the summary of the results at various concentrations studied in the same solvent by us are given below. X=molar fraction of the solvent; r=the surface tension of the solution in dynes per c.m; d=the density of the solution, Pm=the parachor of the solution and Px=the parachor of the solute.

Parachor of Compounds Forming Strong Hydrogen Bonds

1. Methyl Salicylate

Solvent	*x*	*t°c*	*d*	*r*	*Pm*	*Px*
Benzene	.2279	33	.9559	30.4	233.25	323.6
	.2543	33	.9634	30.5	286.26	223.5
	.3085	32	.9860	32.1	243.52	323.2
	.3447	33	.9942	31.5	246.80	323.4
Chloroform	.2208	30	1.376	29.2	213.97	323.2
	.2721	30	1.361	30.3	221.46	322.8
	.3159	30	1.339	30.2	227.60	322.9
	.3601	30	1.329	31.4	233.60	323.4
Cabon tetra chloride	.3077	30	1.425	29.8	251.28	322.9
	.3464	30	1.408	30.4	255 50	323.6
	.3957	30	1.388	31.2	260.80	324.1
	.4603	30	1.360	31.8	267.30	323.4
Toluene	.2196	29	.9358	29.5	262.16	323.4
	.3034	29	.9595	30.5	268.94	323.9
	.3502	29	.9870	32 0	272.60	323.8
	.4245	29	1.0060	32.1	278.40	323.5
Dioxane	.3012	34	1.076	34.4	241.45	323.5
	.3387	29	1.093	36.1	245.90	323.9
	.3825	29	1.097	39.4	251.10	323.6
	.4891	29	1.111	36.2	263.40	323.3
Ethyl acetate	.3216	26	1.010	29.3	250.30	323.5
	.3922	26	1.023	29.2	257.80	323.1
	.4354	26	1.043	31.1	262.40	322.9
	.4863	26	1.056	31.8	268.00	323.4
Methyl acetate	.2175	30	1.003	28.6	208.76	323.9
	.2661	25	1.028	30.0	215.84	323.8
	.3144	25	1.040	30.4	222.60	322.7
	.3842	25	1.057	31.4	232.90	322.9
Acetone	.1982	24	.9158	23.0	183.46	323.8
	.2634	29	.9421	29.3	204.51	323.5
	.3362	24	.9670	30.4	216.10	323.1
	.3758	24	.9970	32.0	222.60	323.4

2. *Salicylaldehyde*

Solvent	*x*	*t⁰c*	*d*	*r*	*Pm*	*Px*
Benzene	.1676	31	.9194	29.2	216.51	266.1
	.1830	31	.9264	30.1	217.73	267.3
	.2309	31	.9430	30.8	220.57	267.1
	.2549	31	.9548	31.6	221.75	266.2
Chloroform	.2200	30	1.403	30.7	201.49	266.8
	.2433	30	1.381	30.0	203.35	266.5
	.2646	30	1.373	30.2	205.06	266.2
	.2865	30	1.353	29.6	206.92	266.4
Carbon tetrachloride	.1995	30	1.488	28.5	229.00	266.2
	.2939	30	1.430	28.6	233.29	266.4
	.3598	35	1.310	30.1	236.40	266.5
	.3839	35	1.402	30.4	237.40	266.3
Toluene	.2360	30	.9296	30.2	250.05	266.3
	.2887	30	.9441	30.7	251.11	266.0
	.3529	30	.9614	31.3	252.53	366.2
	.3858	30	.9620	30.5	253.10	266.1
Dioxane	.2207	35	1.043	32.9	219.26	266.3
	.2497	30	1.064	35.3	221.08	266.3
	.2996	30	1.070	35.4	223.36	266.0
	.3535	30	1.078	36.2	227.55	267.2
Methyl ethyl-ketone	.2425	31	.8999	28.0	215.23	266.5
	.2839	31	.9131	28.3	218.03	266.4
	.3249	31	.9311	29.6	221.32	266.8
	.3585	31	.9432	29.8	223.01	266.1
Ethyl acetate	.2821	31	.9745	27.7	229.96	266.4
	.3361	31	.9888	28.6	232.76	266.4
	.3690	31	1.005	30.1	234.29	266.1
	.4304	31	1.016	30.4	237.40	266.1

Compounds forming weak Hydrogen bonds

1 *o—Cresol*

Benzene	.3151	33	.9311	30.8	222.47	257.0
	.3272	32	.9294	30.9	223.03	256.8
	.4298	33	.9376	30.6	228.30	257.1
	.4472	33	.9426	31.2	229.30	257.6
Chloroform	.2177	30	1.294	23.6	119.18	257.2
	.2631	30	1.314	27.3	202.57	257.2
	.2978	30	1.329	29.9	204.99	256.9
	.3301	30	1.353	34.8	207.54	257.3
Carbon tetra-chloride	.3835	30	1.355	29.3	234.18	257.8
	.4265	30	1.330	29.6	235.60	257.4
	.4372	30	1.320	32.3	236.20	257.9
	.5130	30	1.231	35.6	258.60	257.5
Toluene	.3184	30	.9082	29.2	248.79	256.9
	.3429	30	.9196	30.3	249.00	257.3
	.3681	30	.9219	30.3	249.36	256.9
	.4187	30	.9335	31.0	249.90	256.8

Solvent	*x*	*t°c*	*d*	*r*	*Pm*	*Px*
Methyl ethyl-ketone	.2874	30	.8833	28.6	215.81	257.9
	.3420	30	.8986	29.4	218.62	256.8
	.3968	30	.9095	30.0	221.10	257.5
	.4083	30	.9109	30.1	222.90	257.5
Ethyl acetate	.3062	26	.9484	28.0	228.49	257.6
	.3787	26	.9594	29.0	231.50	257.4
	.3939	26	.9654	29.8	232.10	257.4
	.4760	26	1.0220	36.9	235.40	257.1
Methyl acetate	.2300	26	.9623	27.6	195.17	256.8
	.2910	26	.9714	28.7	200.24	357.5
	.3656	26	.9804	29.7	205.99	256.8
	.4293	26	.9873	30.5	211.10	256.6
Acetone	.2133	24	.8714	28.6	182.37	257.2
	.2719	24	.8904	29.7	187.82	256.8
	.3481	24	.9122	31.2	195.26	257.6
	.3850	24	.9204	31.4	198.94	258.0
2 *O—mono chlorophenol*						
Benzene	.2695	33	.9766	30.0	219.16	255.0
	.3065	33	.9911	30.4	221.40	255.2
	.3293	33	1.0020	30.9	223.44	256.1
	.3410	33	1.0080	31.3	222.65	255.3
Chloroform	.1592	30	1.425	27.7	194.80	255.5
	.2228	30	1.408	28.1	199.03	255.1
	.2763	30	1.394	29.1	202.95	255.4
	.3360	30	1.380	29.8	207.28	255.3
Crabon tetra-chloride	.2719	29	1.482	24.5	247.14	255.1
	.3223	29	1.464	24.7	231.11	255.4
	.3790	29	1.447	30.3	233.77	256.1
	.3974	29	1.438	30.1	234.10	256.4
Toluene	.2778	30	.9594	29.2	247.71	254.9
	.3087	30	.9634	28.6	248.11	255.3
	.3570	30	.9947	30.7	248.70	255.5
	.4027	30	1.0130	31.1	248.90	254.8
Methyl ethyl-ketone	.2734	30	.9513	29.4	214.32	255.4
	.3150	30	.9690	31.1	216.64	255.4
	.3657	30	.9879	29.9	219.40	255.2
	.3944	30	1.0160	31.9	220.80	254.7
Ethyl acetate	.2650	26	1.006	27.9	225.99	254.6
	.3154	26	1.027	29.0	227.94	254.4
	.3736	26	1.052	30.1	230.05	254.2
	.4356	26	1.070	29.1	232.70	254.9
Methyl acetate	.2079	26	1.020	28.3	193.07	255.3
	.3161	26	1.060	29.8	201.22	254.1
	.3780	26	1.086	31.4	206.35	255.2
	.4411	26	1.110	32.7	211.27	255.0
Acetone	.2104	23	.9333	29.4	181.73	255.9
	.2711	23	.9681	30.5	187.44	256.1

Solvent	*x*	t^0c	*d*	*r*	*Pm*	*Px*
	.3559	23	1.0160	32.4	195.16	255.3
	.4040	23	1.0420	33.4	199.54	255.1
3. *Pyrogallol.*						
Dioxane	.0618	33	1.053	35.4	209.28	258.7
	.0819	28	1.064	36.4	210.22	258.0
	.0901	28	1.067	36.5	210.75	257.9
	.1004	28	1.083	35.6	207.05	258.4
Ethyl alcohol	.0786	35	.8798	28.3	137.22	258.7
	.0955	30	.9003	29.7	139.47	257.3
	.1136	30	.9133	30.3	141.60	257.2
	.1243	30	.9237	31.0	143.09	258.2
Acetone	.0661	29	.8439	26.6	168.35	257.8
	.0823	29	.8576	27.5	169.89	257.6
	.0901	29	.8700	28.6	170.61	257.5
	.0973	29	.8818	29.8	171.30	258.1
Methyl acetate	.1019	30	.9860	27.8	184.94	257.5
	.1262	30	1.001	29.0	186.98	258.3
	.1455	30	1.013	29.9	183.57	258.2
	.1647	30	1.023	30.8	190.19	257.8
Ethyl acetate	.0799	30	.9640	28.8	219.08	257.7
	.1475	30	.9858	29.7	221.89	257.6
	.1752	30	.2919	29.8	223.02	258.1
	.1976	30	.9995	31.4	226.45	257.8
4—*meta-Dihydroxy Benzene (Resorcinol).*						
Dioxane	.1379	29	1.064	36.7	210.57	239.0
	.1632	29	1.068	36.7	211.34	238.5
	.1950	29	1.080	38.0	212.48	238.8
	.2248	29	1.086	38.8	213.49	239.3
Ethyl alcohol	.1187	29	.8933	29.6	140.21	239.3
	.1248	29	.8971	29.7	140.82	238.7
	.1311	29	.9031	30.4	141.72	238.8
	.1914	29	.9253	30.6	148.25	239.2
Acetone	.1041	30	.8547	27.3	170.06	239.7
	.1367	30	.8742	28.4	172.52	239.5
	.1708	30	.8954	30.3	175.34	239.7
	.1936	30	.9057	30.8	176.98	239.5
Methyl acetate	.1330	30	.9759	27.5	185.10	239.8
	.1519	30	.9924	29.2	186.28	239.5
	.1718	30	.9956	29.4	187.42	239.3
	.2040	30	1.016	31.3	189.45	239.0
Ethyl acetate	.1571	31	.9677	28.9	219.42	239.5
	.2206	31	.9795	29.3	220.79	238.8
	.2417	31	.9863	29.9	221.44	239.2
	.2483	31	.9881	30.0	221.33	238.5
Methyl ethyl ketone	.2059	35	.9042	16.5	178.04	239.8
	.2402	30	.9274	18.1	180.63	239.5
	.2780	30	.9315	18.2	183.26	238.7
	.2796	30	.9456	19.4	133.50	239.0

5. *para—Dihydroxy Benzene* (*Hrdroquinone*)

Solvent	*x*	$t^{o}c$	*d*	*r*	*Pm*	*Px*
Dioxane	.0396	29	1.037	34.2	207.29	237.1
	.0531	29	1.042	36.5	207.76	238.3
	.0706	29	1.047	35.5	208.17	237.5
	.0828	29	1.052	36.7	208.14	237.2
Ethyl alcohol	.0780	29	.8620	27.2	135.35	236.5
	.0856	29	.8720	28.2	136.26	236.6
	.1064	29	.8804	28.3	138.49	236.8
	.1227	29	.8894	28.7	140.39	237.0
Acetone	.0765	29	.8354	26.1	167.76	237.4
	.0975	29	.8484	27.2	169 31	237.0
	.1176	29	.8628	27.8	170 84	236.8
	.1225	29	.8638	27.7	171.17	236.9
Methyl acetate	.0951	29	.9450	26.6	184.25	238.1
	.1114	29	.9745	27.5	183.52	238.1
	.1267	29	.9788	27.8	185.11	237.6
	.1610	29	.9947	29.2	186.65	238.2
Ethyl acetate	.0921	31	.9285	25.4	217.75	238.2
	.1004	36	.9279	25.1	217.88	237.8
	.1133	31	.9374	25.5	217.05	236 9
	.1389	31	.9456	26.5	218.07	236.9
Methyl ethylketone	.2164	30	.9141	30.9	207.16	237.1
	.2329	30	.9202	31.5	207.80	237.5
	.2552	30	.9317	32.1	208.85	236.9
	.2638	30	.9380	32.5	209.09	237.6

6. *meta—Nitrophenol*

Benzene	.0175	31	.8784	28.3	207.69	274.3
	.0191	32	.8800	28.4	207.83	273.8
	.0233	37	.8786	28.3	208.11	274.2
	.0517	30	.8969	28.9	209.97	274.1
Dioxane	.0816	35	1.054	34.4	211.58	274.1
	.0947	35	1.061	34.7	212.43	273.8
	.1133	29	1.069	35.3	213.78	274.1
	.1277	29	1.077	35.8	214.61	273.1
Methyl acetate	.0878	30	.9729	26.1	185.26	274.1
	.1186	30	.9959	27.7	188.28	273.9
	.1310	30	1.001	28.2	189.55	274.4
	.1461	30	1.014	29.0	191.01	274.6
Methyl ethylketone	.1037	28	.8690	26.7	206.64	274.2
	.1307	28	.8872	27.5	208.65	273.4
	.1497	33	.8954	27.5	209.99	273.7
	.3898	28	.9674	28.0	228.10	273.7
Ethyl acetate	.1150	30	.9537	25.9	222.30	273.8
	.1266	30	.9594	26.3	223.03	273.7
	.1554	35	.9623	25.7	224.80	273.8
	.1715	35	.9795	27.0	225.82	274.2

7. *para—Nitrophenol*

Solvent	*x*	*t°c*	*d*	*r*	*Pm*	*Px*
Methyl ethylketone	.1269	30	.8843	27.3	208.33	273.8
	.1441	30	.8956	27.8	209.63	273.7
	.1735	30	.9139	28.6	211.91	273.8
	.1847	30	.9206	28.8	212.56	273.1
Ethyl alcohol	.0732	29	.8738	26.7	137.67	274.1
	.0853	34	.8814	26.8	139.36	273.8
	.0923	29	.8925	27.6	140.37	273.8
	.0971	29	.8991	28.1	141.06	273.5
Acetone	.0724	31	.8433	25.5	170.16	274.1
	.0742	31	.8474	25.8	170.34	274.1
	.1031	31	.8788	27.2	173.56	273.8
	.1899	31	.9193	27.7	183.15	273.6
Methyl acetate	.0601	30	.9576	25.2	132.34	273 6
	.0614	30	.9588	25.4	132.75	274.2
	.0707	30	.9596	25.2	183.60	273.3
	.0862	30	.9718	26.0	185.80	273.8
Ethyl acetate	.0839	30	.9374	25.1	220.50	274.5
	.0996	30	.9456	25 6	221.51	273.7
	.1196	30	.9523	25 6	222.53	272.9
	.1386	30	.9625	26.2	223.67	273.4

SUMMARY

Compounds Forming Strong Hydrogen Bond

Substance	*Calculated Value*	*Observed Value*	*Difference in Value*
Methyl salicylate	334.1	323.7	10.4
Salicylaldehyde	275.1	266 5	8.6
O-Nitrophenol	285.7	272.9	12.8
Acetic acid (Dimer)	282.2	260 0	22.2
Propionic acid "	360.2	340.0	20.2
Benzoic acid "	550.0	537.0	13 0

Compounds Forming Weak Hydrogen Bond

O-Cresol	266.1	257.3	8.8
O-mono Chlorophenol	265.7	255.2	10.5
Pyrogallol	267.1	257.9	9.2
Resorcinol	247.1	239.2	7.9
Hydroquinone	247.1	237.4	9.7
meta-Nitrophenol	285.7	273.9	11.8
p-Nitrophenol	285.7	273.7	12.0

DISCUSSION

Compounds forming strong hydrogen bond :— The calculated parachors of methyl salicylate and salicylaldehyde are 334.1 and 275.1, while our observed values are 323.7 and 266.5. Sidgwick and Bayliss (6) and Gibling (7) have also observed almost the same values for them in pure state. Thus there is a fall of 10.4 and 8.6 respectively. S. G. Khandekar and W. V. Bhagwat have observed (8) the parachor of o-Nitrophenol in liquid state in several solvents. Their observed value is 285.7. Thus there is a fall of 12.8 in o-Nitrophenol. Bhagwat, Shukla and Khandekar (1) have studied hydrogen bond formation from the study of parachor of carboxylic acids. They have obtained the average value for each hydrogen bond in acetic acid, propionic acid and benzoic acid as 12, 11 and 6 respectively.

Compounds forming weak hydrogen bond :— The calculated parachors of o-cresol, o-mono chlorophenol, pyrogallol, resorcinol and hydroquinone are 266.1, 265.7, 267.1, 247.1 and 247.1 respectively. Our observed values for them are 257.3, 255.2, 257.9, 239.2 and 237.4. Thus there is a fall of 8.8, 10.5 9.2, 7.9 and 9.7 respectively. The parachor for meta-nitrophenol and para-nitrophenol is 285.7, while our observed values are 273.9 and 273.7. The fall in parachor therefore is 12. Bhatnagar and Singh (9) and Sidgwick and Bayliss (6) have also observed the parachor of para and meta nitrophenols in pure state as 283.2 and 283.3. But these values are higher in fused state. These values are higher because the hydrogen bond might have been ruptured in the fused state.

Our observations clearly show that the parachor values fail to distinguish a strong hydrogen bond from a weak hydrogen bond. It may therefore be concluded that the parachor method can determine the hydrogen bond formation but is inadequate to determine the strength of hydrogen bond. It is further to be noted that all these compounds can have alternative resonance structure (1). But in that case the fall in parachor should be small. The fact that the drop in parachor is sufficiently large indicates hydrogen bond structure for these compounds, since it is mainly ionic in nature.

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AN INJECTION TECHNIQUE FOR STUDY OF THE BLOOD VESSELS OF THE HEART

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As the visualisation of the finest branches of arteries by injection followed by dissection has its own limitations, various workers have taken to roentgenography after injection of some radio-opaque substance. A radio-opaque mass for injection should preferably have a high degree of radio-opacity and should be economical at the same time. It should not stain the surrounding tissues, but should remain within the lumen of the injected vessels.

The radio-opaque substances employed in vascular injection studies may be divided into the major categories: (1) minerals, their salts and their oxides and (ii) organic dyes.

Of minerals and mineral oxides, Gough (1920) recommended barium sulphate, pointing out the advantages of the method in permitting routine X'ray examination of the vascular system of man. Hill (1924) reported the use of barium oxychloride in a radio-opaque injection mass. The use of metallic mercury has met with approval in many laboratories, while cinnabar or mercuric oxide in water suspension has been employed by Batson (1939) and by Swindle (1940) with great success. J. C. Sinclair got outstanding success with vermilion (red mercuric sulphate) in saline. Red lead oxide (lead tetra oxide) has been employed by various investigators as early as 1896-viz., by Davis and many others following him. Kellner (1934) and later Epstein (1944) devised an injection mass containing both lead nitrate and aluminium acetate, while others have used lead phosphate with good results.

The use of radio-opaque organic dyes came with the introduction of latex as an injection medium. However the high cost of such a material limited its use in vascular investigations on a large scale.

The various menstruums employed for injecting the radio-opaque masses are Saline, Agar, Gelatine, Starch, Linseed oil, Shellac, Bees wax, Glycerine, Acacia, Latex etc.

For the investigation of the blood vessels of the heart we have been using with outstanding success a radio-opaque injection mass, which is not only simple and efficient, but can be easily prepared and is cheap. To demonstrate the exact territories of left and right coronary arteries, two differently coloured injection materials—red and blue—were prepared as follows:
Red Solution (A)—for left coronary artery:—

Red Lead ... 1 part

Starch Powder	2 parts
Distilled Water	Double the quantity of powder.

Shake vigorously and filter through three layers of guaze.

Blue solution (B) —for right coronary artery:—

Lead acetate 35% solution	100 c.c.
Sodium Phosphate 4% solution	70 c.c.
Phenol red. 0.06%	1 c.c.
Sodium Hydroxide 10%	25 c.c.

Add sodium hydroxide till a faint pink colour is obtained, indicating that the solution is neutral.

Boil the mass for 10 minutes till lead phosphate precipitates. Then strain through three layers of guaze. Finally add prussian blue to colour it blue.

Injection Apparatus and method of injecting the coronary arteries.

It is essential that the injection mass should be injected at a regulated constant pressure so as to get a constant flow; at the same time the pressure should not be so high as to rupture the minute vessels. As this could not be effected by use of an ordinary syringe, a special apparatus (Fig. 1) which fulfils all the essential requirements has been devised by us.

Hearts from fresh cadavers are removed without injury to the blood vessels. Fresh specimens may be satisfactorily injected even though a few hours have passed after removal, but hearts in which putrefactive changes have set in are definitely unsuitable. The glass canulae are inserted into the openings of the coronary arteries, and tied by purse string sutrues. To remove the air, they are filled in with water or the injecting solution and, when all air bubbles have been excluded, the heart is connected with the injecting apparatus. The manometric device is adjusted at a maximum pressure of 150 mm. of mercury before connecting to the coronary vessels. This is controlled by a safety device wherein the glass tube *X* is kept under mercury up to 150 mm. The injection is made by pressing the bulb *O*, and the pressure maintained automatically by the safety device *X*. The warming of the water bath was not necessary in case of the solutions used, as the vessels could be injected at room temperature.

When the injection is complete, which can be easily ascertained with the help of a hand-lens, the openings of coronary arteries are tied and the canulae removed. It is essential that the canulae should not be inserted deeply into the lumen of the arteries, lest the origin of any small branch arising just beyond the coronary orifice should be blocked.

Technique for X'ray:

In our study the heart was opened for X'ray by the Schlesinger's method which unrolls the different chambers in one plane without damage to the coronary arteries. The method consists in incising the heart through the anterior wall of the pulmonary opening and then along the right side of the anterior interventricular groove close to the anterior attachment of the septum till the apex is reached. This is followed by a second incision which cuts in between the two anterolateral aortic cusps, thereby protecting the orifices of both the coronary arteries. The incision includes the posterior wall of the pulmonary ring and extends to the base of the interventricular septum for 1 cm. The anterior and posterior attachments of the septum, including its anterior and posterior basal parts were completely severed by two more incisions. The latter started from the lowest point of the above incision—one extending forwards and downwards along the anterior border of the septum and the other backwards and downwards along its posterior attachment, both meeting at the apex and thus completely removing the septum. The left atrium is opened by an incision that cuts through the anterior cusp of the mitral valve and ring, then extends along the left side of the inter-atrial septum to the opening of the pulmonary veins. The right atrium is opened by an incision passing in between the anterior and medial cusps of the tricuspid valves. After the tricuspid ring is cut lengthwise the incision is continued on to the posterior wall of the aortic ring, thereby separating the coronary openings to either side. The incision is further extended along the right side of interatrial septum so as to reach the opening of the superior vena cava, thus completely unrolling the heart. The heart is now spread out on a paper over the cassette containing the X-ray film with the pericardial surface in contact with it. The most satisfactory results were obtained by an exposure of 1/10 seconds, using 90 Volts and 10 M. A. The target film distance was 36". We have obtained excellent results not only on human heart but also on the hearts of goat, sheep and dog. The X'ray of the human heart is shown in Fig. 2.

SUMMARY

Lead in the form of red lead and lead phosphate has been found to be an excellent contrast medium for roentgenographic study of the blood vessels of the heart. The smallest arterioles and venules can be visualised on X-ray films with lead suspension injected by the apparatus described.

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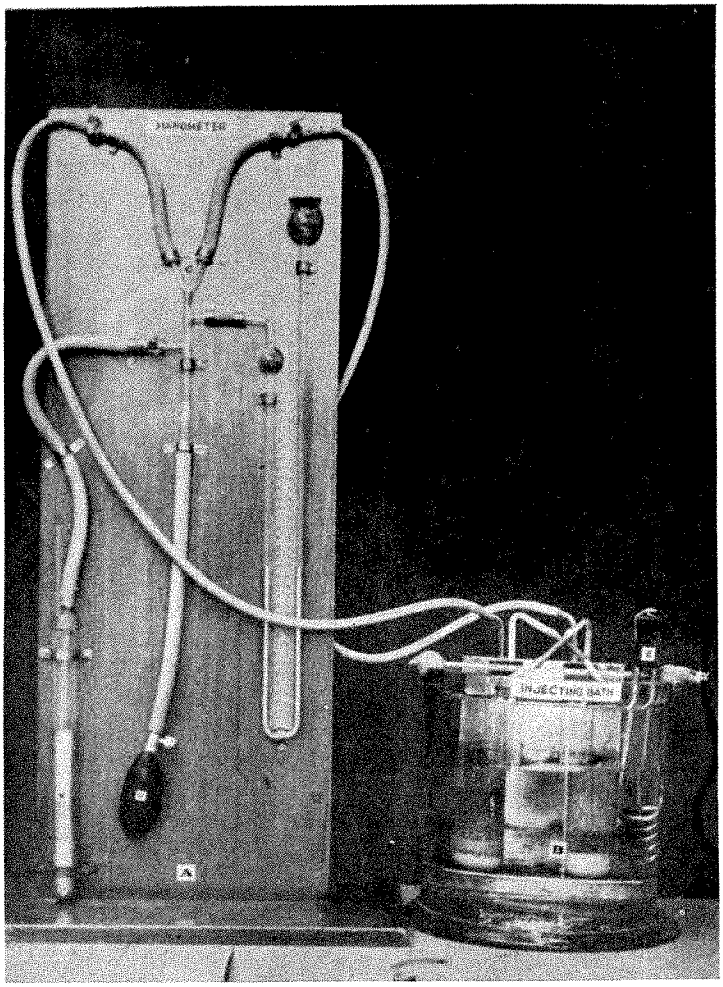

Fig. 1. *A* is the mercury manometer reading up to 200 mm., with safety device *X*, pumping bulb *O* and a Y-shaped tube *C*. One end of the Y-shaped tube is connected with the pump and other two ends by two rubber tubes to the injecting reservoirs in water-bath *B*. The bath contains a stand, on which two test tubes containing different injection solutions are placed. These test tubes are fitted with glass tubings and canulae. The temperature of the bath, if necessary can be regulated by the electric immersion heater *E*.

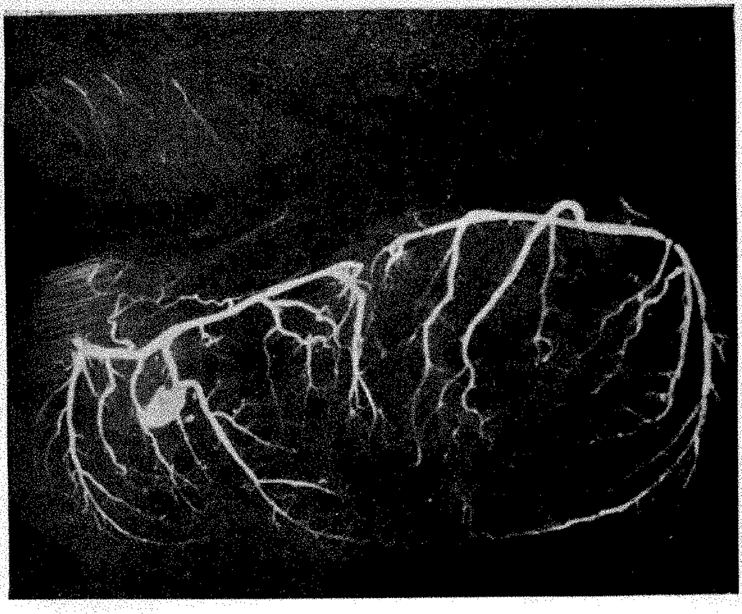

Fig. 2. X'ray plate of the injected coronary arteries of a human heart.

ON THE FORMATION AND STABILITY OF ACID CARBONATES OF METALS OTHER THAN ALKALI METALS.

Part II

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A complete analysis of some of the precipitated bicarbonates of divalent cations like manganese, cobalt, zinc, cadmium and mercury (ic) has been carried out and it has been found that they are definite bicarbonate hydrates and that an extra amount of water or carbon-dioxide seems to be necessary for the stability of the bicarbonates.

In part I of the series has been described the isolation of some of the acid carbonates of metals. In order to advance the study of these compounds, an attempt has now been made to determine the formulae of the precipitated bicarbonate hydrates of divalent cations like manganese, cobalt, zinc, cadmium and mercury (i-c).

EXPERIMENTAL

The bicarbonates were prepared by double decomposition method i. e. addition of $KHCO_3$ to the soluble salts of metals in the neighbourhood of O°C and the product did not decompose at room temperature when kept in an atmosphere of carbon-dioxide. The formulae of the hydrated precipitates have been determined by keeping them in an atmosphere of dry CO_2 until the weight became constant when it was weighed quickly and, then, analysing the product for the ratio; Oxide: CO_2 : H_2O.

The ratio of the weights of CO_2 to the oxide in these precipitates was determined as mentioned in part. I. The weight of water in the hydrated precipitate was known by difference.

The ratio of the molecules of oxide, CO_2 and water was calculated as under :—

$$\frac{\text{Wt. of Oxide}}{\text{Mol. Wt. of Oxide}} = \frac{\text{Wt. of } CO_2}{\text{Mol. Wt. of } CO_2} = \frac{\text{Wt. of Water}}{\text{Mol. Wt. of Water}}$$

The results that follow show that the samples of Manganese Bicarbonate kept in dry CO_2 remain in a stable condition—it decomposes in vacuum or even in ordinary air. This change can also be followed by the colour development from white to brown—sunlight has not much effect if the sample is protected by an atmosphere of CO_2.

Samples of Manganese Bicarbonate placed in an atmosphere of dry CO_2

No.	Wt. of dried ppt. of HCO_3.	Wt. of MnO	Wt. of CO_2	Wt. of Water (By diff.)	Formula.
(1)	0.3760	0.0964	0.1302	0.1494	
		$\frac{0.0964}{71}$	$\frac{0.1302}{44}$	$\frac{0.1494}{18}$	

	gm. mols.	0.00136	0.00297	0.00829	MnO. $2.18CO_2.6.09H_2O$
	Ratio	1	: 2.18	: 6.09	
(2)	0.2246	0.0578	0.0786	0.0882	
	gm. mols.	0.00081	0.00178	0.00490	MnO. $2.19CO_2.6.04H_2O$.
	Simplest Ratio	1	: 2.19	: 6.04	
(3)	0.2082	0.0534	0.0724	0.0824	
	gm. mols.	0.00075	0.00164	0.00457	MnO. $2.18CO_2.6.09H_2O$.
	Simplest Ratio	1	: 2.18	: 6.09	

Mean Value & Formula: MnO. $2.18\ CO_2.\ 6.07\ H_2O$
OR
Mn $(HCO_3)_2.\ 5\ H_2O$.

Samples of Manganese Bicarbonate placed in Vacuum.

No.	Wt. of ppt alone after Wt. has become constant.	Wt. of MnO.	Wt. of CO_2	Wt. of Water (by diff.)	Formula
(1)	0.2790	0.0882	0.0568	0.1340	
	gm. mols	$\frac{0.0882}{71}$	$\frac{0.0568}{44}$	$\frac{0.1340}{18}$	
	gm. mols.	0.00124	0.00129	0.00744	MnO. $1.04CO_2.\ 6.00H_2O$.
	Simplest Ratio	1	: 1.04	: 6.00	
(2)	0.3358	0.1049	0.0703	0.1606	
	gm. mols.	0.00147	0.00159	0.00892	MnO. $1.08\ CO_2.\ 6.06H_2O$.
	Simplest Ratio	1	: 1.08	: 6.06	

(Obviously the bicarbonate is decomposed to $MnCO_3.\ 6H_2O$)

Samples of Manganese Bicarbonate placed in Ordinary Desiccator.

(1)	0.7704	0.1191	0.0862	0.5651	
		$\frac{0.1191}{71}$	$\frac{0.0862}{44}$	$\frac{0.5651}{18}$	
	gm. mols.	0.00167	0.00196	0.0314	MnO. $1.17\ CO_2.18.80H_2O$.
	Simplest Ratio	1	: 1.17	: 18.80	
(2)	0.4476	0.0696	0.0506	0.3274	
	gm. mols.	0.00098	0.00115	0.01819	MnO. $1.17\ CO_2.\ 18.56H_2O$.
	Simplest Ratio	1	: 1.17	: 18.56	

(No Stoichiometric relation with respect to water.)

Thus, it was conclusively proved that samples of Manganese Bicarbonate can be kept in an atmosphere of dry CO_2 in a stable condition thus making it possible to determine the formula of the hydrated precipitate. The method was, then, extended to the study of the formulae of the precipitated bicarbonate hydrates of divalent cations like cobalt, zinc, cadmium and mercury (-ic). In these cases, a complete analysis of the bicarbonate hydrates has been carried out with a view to determine their formulae. It has been found that they are definite bicarbonate hydrates having the composition indicated below :—

(1) MnO 2.18 CO_2 . 6.05 H_2O i. e. Mn $(HCO_3)_2$ $5H_2O$.
(2) CoO 2.01 CO_2 . 6.08 H_2O i. e. Co $(HCO_3)_2$ $5H_2O$.
(3) ZnO 2.73 CO_2 . 1.03 H_2O i. e. Zn $(HCO_3)_2$ 0.73 CO_2.
(4) CdO 2.73 CO_2 . 2.19 H_2O i. e. Cd $(HCO_3)_2$ 0.73 CO_2H_2O.
(5) HgO 2.11 CO_2 . 3.12 H_2O i. e. Hg $(HCO_3)_2$ 2 H_2O.

Attempts at preparation of the bicarbonates by Black's Method (Absorption of H_2CO_3 by the carbonates of the corresponding metals) did not give stable bicarbonates because they do not contain the necessary amount of water of crystallisation (which is apparently necessary for their stability). Further it was observed that the products of absorption of H_2CO_3 by carbonates are very unstable which decompose as soon as one of the reactants (here, for example, moisture is removed).

$$MnCO_3 + CO_2 + H_2O \rightleftharpoons Mn\,(HCO_3)_2$$

The precipitation method yields bicarbonate hydrates which are comparatively more stable.

The results suggest that an extra amount of water or carbon-dioxide seems to be necessary for the stability of the bicarbonates.

ACKNOWLEDGEMENT

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STUDIES ON THE COMPOSITION AND COLLOIDAL BEHAVIOUR OF THE FERROCYANIDES OF SOME METALS.

PART I. COMPOSITION OF COBALT FERROCYANIDE BY CONDUCTOMETRIC, POTENTIOMETRIC AND THERMOMETRIC METHODS.

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AND

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Composition of cobalt ferrocyanide has been investigated by conductometric, potentiometric, and thermometric methods by titrating cobalt chloride solution with K_4FeCy_6 both in aqueous and aqueous alcoholic medium. Direct titrations *i.e.* $CoCl_2$ from the burette added to K_4FeCy_6 while reverse titrations (K_4Fecy_6 from the burette added to $CoCl_2$) show the existence of a compound $K_2CoFeCy_6 \cdot Co_2FeCy_6$ or $K_2Co_3(FeCy_6)_2$. The composition of this complex has been found to be influenced by adsorption and hydrolysis.

The composition of cobalt ferrocyanide was investigated by a number of workers both by analytical and physico-chemical methods. *Wyrubow*[9] observed that on adding potassium ferro cyanide to a cobalt salt solution, a blue precipitate, which soon changes to reddish colour in air is formed. But the exact composition of the precipitate could not be determined on the result of his experiments. He suggested that cobalt ferrocyanide under varying conditions may correspond to different compositions as given by the formulae CO_2FeCy_6; K_2Co_7 $(FeCy_6)4$; $K_2CoFeCy_6$ and K_6Co_5 $(FeCy_6)_4$.

Atanasiu and Velculescu[1] carried out potentiometric titrations of cobalt and nickel sulphate against potassium ferrocyanide. They observed inflexions on the titration curves at the molecular ratio of five cobalt or nickel and four of ferrocyanide. *Britton and Dodd*[3] employed the method of conductometric titrations to study the precipitates formed by the interaction of a number of metallic salts with potassium ferrocyanide and they obtained inflexion corresponding to the formation of Co_2FeCY_6 XK_4FeCy_6 when $X=0.63$. X-ray diffraction method was used by *Harry B. Weiser, W. O. Milligan*[8]. They observed that the alkali ferrocyanides are adsorbed on the surface of highly dispersed crystals of the complex and no double salt is formed. According to them the breaks in the conductometric titration curves as observed by Britton and Dodd (loc. cit.) are without significance as regards the formation of double salts and may correspond to the flat portion of the adsorption curve. *Bhattacharya and co-workers*[2] have carried out extensive investigations on the composition of a number of metallic ferro-and ferricyanides by conductometric, potentiometric and thermometric titrations. More recently polarographic methods have been used by *Luigi Ricohoni and Paolo Goldschmied*[7], *Khosla and Gaur*[6] to elucidate the composition of some of these complexes.

In view of the conflicting opinions on the composition of cobalt ferrocyanide, it appears that results obtained by several physico-chemical methods may prove more conclusive. In this paper we communicate the results of our investigations by conductometry, potentiometry and thermometry.

EXPERIMENTAL

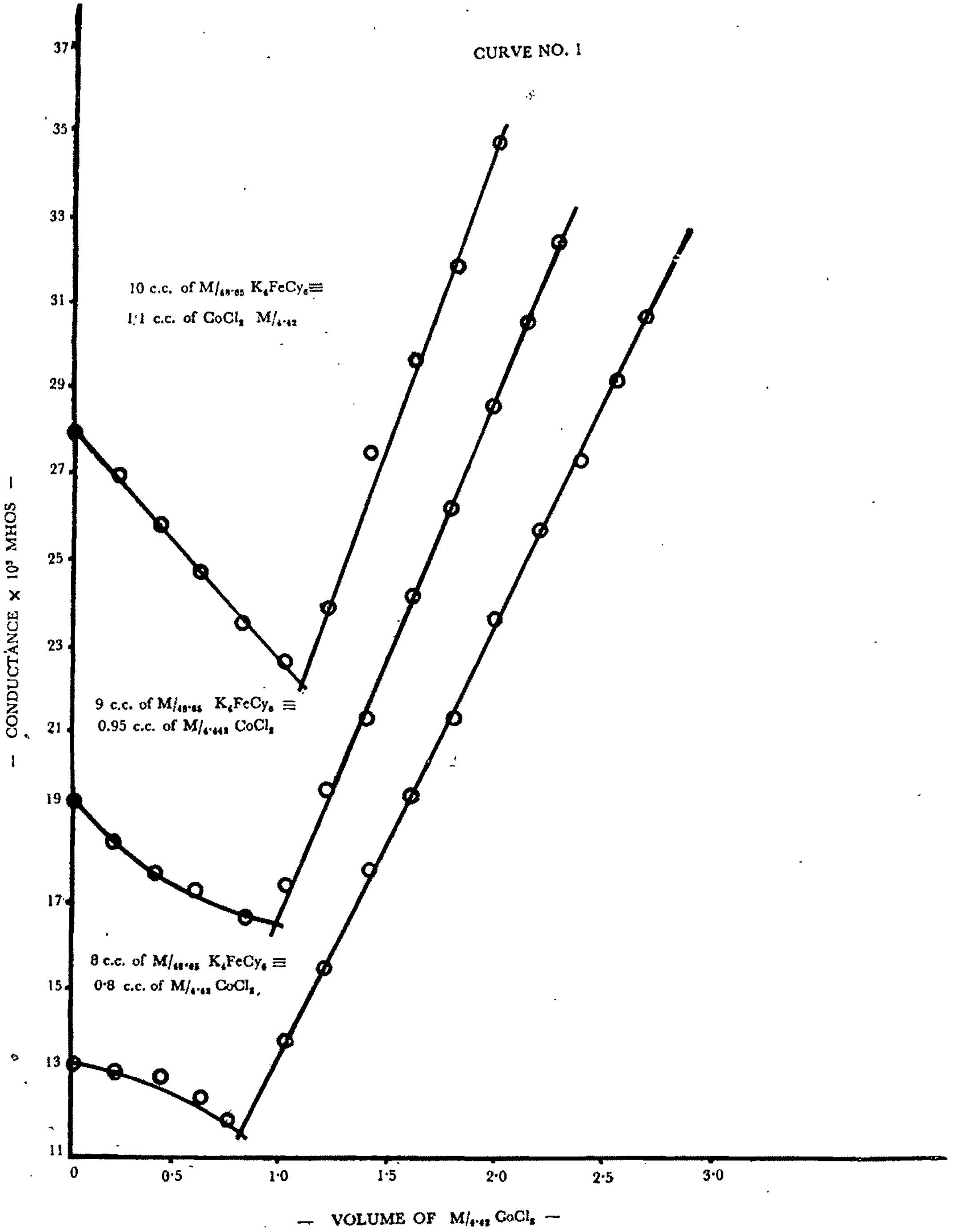
The method used by *Gaur and Bhattacharya*[4] in carrying out the conductometric and potentiometric titrations and that of Halder[5] for thermometric titrations were followed. In conductometric titrations the end point was determined with the help of Kohlrausch's Universal Bridge (Pye Ltd.). The conductance obtained after each addition of the solution from the burette was corrected for dilution (Davies—The Conductivity of solutions, p. 238). Potentiometric titrations were performed with the help of a potentiometer (Leeds and Northrup). Ferri-ferrocyanide electrode was used and the changes in redox potential given by the equation, $E = Eo + 0.059 \log \frac{FeCy_6 \cdots}{Fecy_6 \cdots\cdot}$ (at 25°C) were carried out in Dewar's flask and the equivalence point was determined by the break or discontinuity in the titration curves. Observations were made in aqueous and aqueous alcoholic medium and these have been tabulated in Tables No. I,II and III. Two typical curves, one in aqueous and the other in aqueous—alcoholic medium, have been given for only one concentration ratio of the reactants, both in direct and reverse titrations, wherever possible (vide curves No. I to 10). When $CoCl_2$ is taken in the burette and added to $K_4Fe(CN)_6$ it has been referred as direct titrations, while the reverse titrations mean the addition of $K_4Fe(CN)_6$ to $CoCl_2$. In order to minimise errors in conductivity titrations due to large volume change the solution taken in the cell was kept atleast 10 times more dilute than the solution taken in the burette.

TABLE I

Direct conductometric titrations

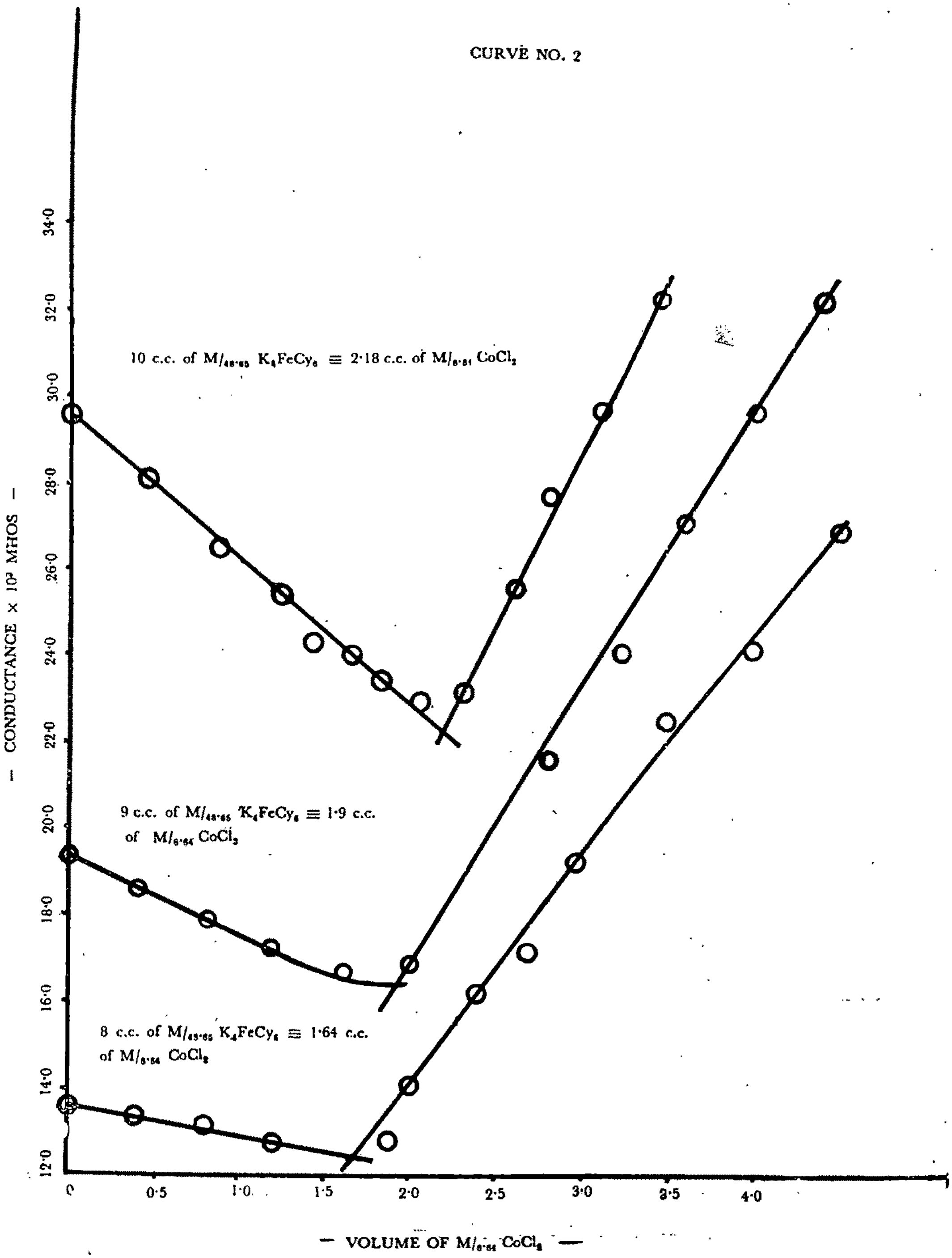
(i) M/4.42 $CoCl_2$ and M/48.65 K_4FeCy_6. Conc. ratio (n) = 1:11.07

Vol. of M/48.65 K_4FeCy_6 in the cell (v)	Alcohol added	Vol of M/4.42 $CoCl_2$ req. for titration curves (v_1)	Vol. of M/4.42 $CoCl_2$ calculated for 10 c.c. of K_4FeCy_6 10x (v_1/v)	Eqv. Vol. of M/48.65
10.0 c.c.	0.0 c.c.	1.10 c.c.	1.10 c.c.	12.2 c.c.
9.0	1.0	0.95	1.05	11.6 Curve 1
8.0	2.0	0.80	1.00	11.0
(ii) M/8.84 $CoCl_2$ and M/48.65 K_4FeCy_6. Conc. ratio (n) = 1:5.53				
1.00 c.c.	0.0 c.c.	2.18 c.c.	2.13 c.c.	12.1 c.c. Curve No. 2
9.0	1.0	1.92	2.13	11.8
8.0	2.0	1.64	2.05	11.3



CURVE NO. 1

10 c.c. of M/48·65 K_4FeCy_6 ≡
1·1 c.c. of $CoCl_2$ M/4·42
9 c.c. of M/48·65 K_4FeCy_6 ≡
0.95 c.c. of M/4·442 $CoCl_2$
8 c.c. of M/48·65 K_4FeCy_6 ≡
0·8 c.c. of M/4·42 $CoCl_2$,
— CONDUCTANCE × 10^3 MHOS —
37
35
33
31
29
27
25
23
21
19
17
15
13
11
0
0·5
1·0
1·5
2·0
2·5
3·0
— VOLUME OF M/4·42 $CoCl_2$ —



CURVE NO. 2

10 c.c. of $M/_{43\cdot65}$ K_4FeCy_6 ≡ 2·18 c.c. of $M/_{8\cdot64}$ $CoCl_2$
9 c.c. of $M/_{43\cdot65}$ K_4FeCy_6 ≡ 1·9 c.c. of $M/_{8\cdot64}$ $CoCl_2$
8 c.c. of $M/_{43\cdot65}$ K_4FeCy_6 ≡ 1·64 c.c. of $M/_{8\cdot64}$ $CoCl_2$
— CONDUCTANCE × 10^3 MHOS —
34·0
32·0
30·0
28·0
26·0
24·0
22·0
20·0
18·0
16·0
14·0
12·0
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
— VOLUME OF $M/_{8\cdot64}$ $CoCl_2$ —

TABLE II

Reverse conductometric titrations

(i) M/4.865 K_4FeCy_6 and M/44.2. $CoCl_2$. Conc. ratio (n) = 1 :9.07

Vol. of M/44.8 $CoCl_2$ in the cell (v)	Alcohol added	Vol. of M/4.865 reqd. (Titration curves (v^1)	Vol. of M/4.865 K_4FeCy_6 calculated for 10 c.c. of M/44.2 $CoCl_2$ $(10v_1/v)$	Eq. Vol. of M/44.2 K_4FeCy_6 n $(10v_1/v)$
10 c.c.	0.0 c.c	0.85 c.c.	0.85 c.c	7.7 c.c. Curve No. 3
9.0	1.0	0.83	0.92	8.3
8.0	2.0	0.80	1.0	9.0
(ii) M/9.73 K_4FeCy_6 and M/44.2 $CoCl_2$. Conc. ratio (n) = 1 :4.53.				
10.0. c.c.	0.0 c.c.	1.70 c.c.	1.70 c.c.	7.7 c.c.
9.0	1.0	1.64	1.82	8.2
8.0	2.0	1.55	1.94	8.8 Curve No. 4

TABLE III

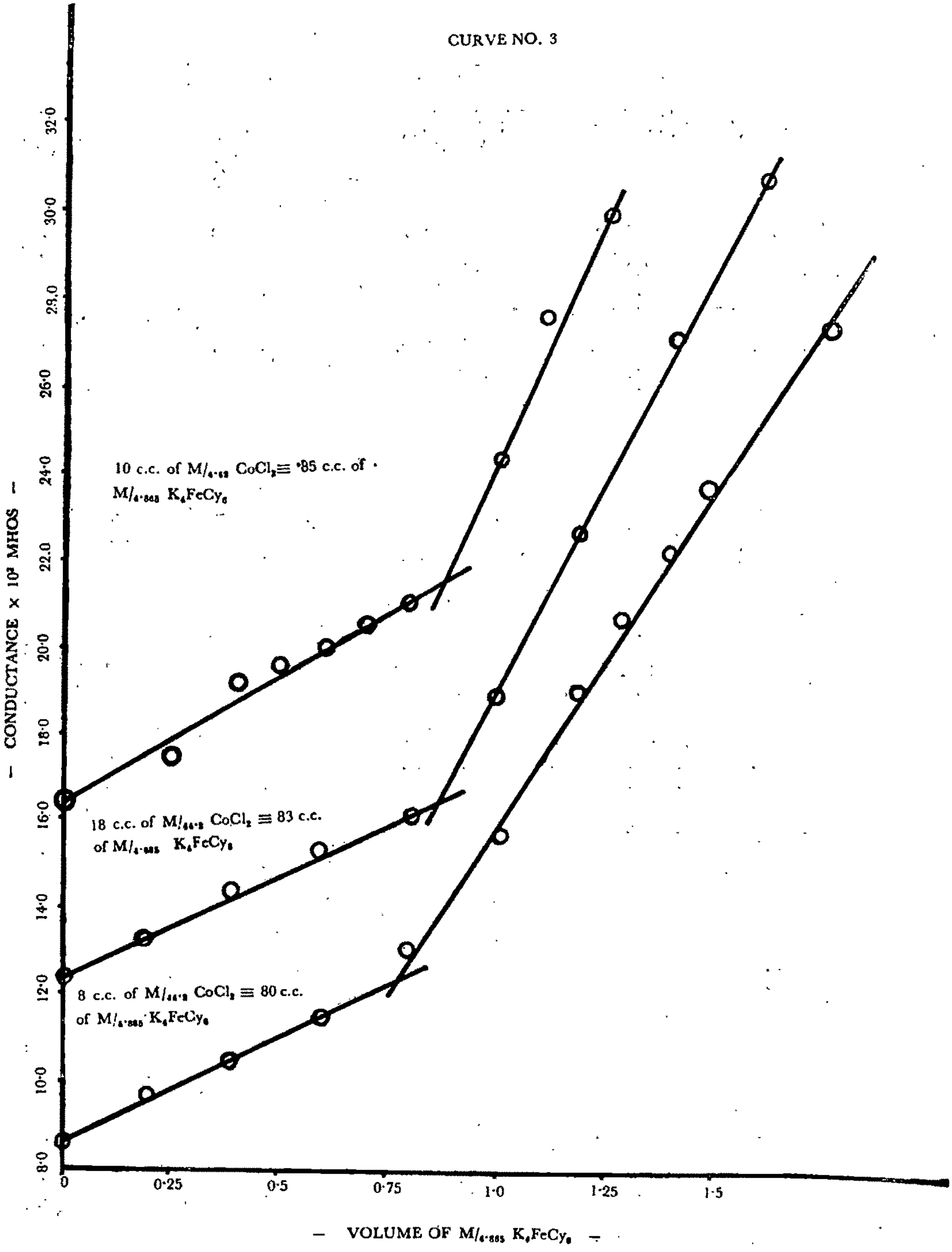
Vol. of M/44.2 $CoCl_2$ in the beaker (v)	Alcohol added	Vol. of M/9.73 K_4FeCy_6 calculated for 20 c.c. of M/44.2 $CoCl_2$ $20(v_1/v)$	Vol. of M/9.73 K_4FeCy_6 reqd. Titration curves (v_1)	Eqv. Vol. of M/44.2. K_4FeCy_6 $n(20v_1/v)$
20.0 c.c.	0.0 c.c.	3.50 c.c.	3.50 c.c.	15.9 c.c. Curve No. 5
18.0	2.0	4.00	3.60 c.c.	18.1
16.0	4.0	4.12	3.40	18.9 Curve No. 6
(ii) M/19.46 K_4FeCy_6 and M/44.2 $CoCl_2$. Conc. ratio = 1 :2.26				
20.0 c.c.	0.0 c.c.	7.00 c.c.	7.0 c.c.	15.9 c.c.
18.0	2.0 c.c.	7.22	6.50 c.c.	16.3 Curve No. 7
16.0	4.0 c.c.	7.50	6.00 c.c.	17.0 Curve No. 8

TABLE IV

Direct thermometric titrations

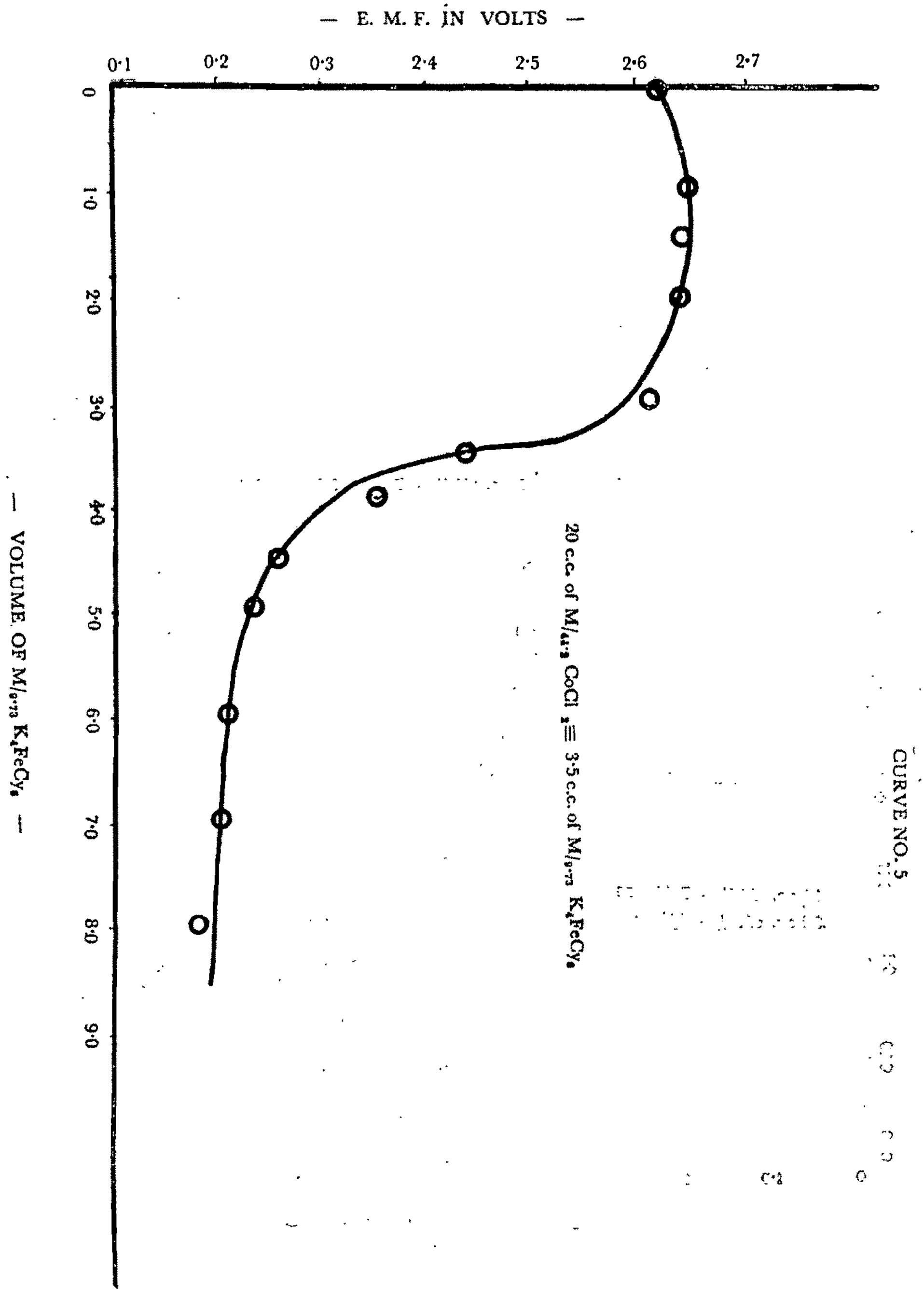
(i) M/4.42 $CoCl_2$ and M/48.65 K_4FeCy_6. Conc. ratio = 1 :11.07

Vol. of M/48.65 K_4FeCy_6 in Dewar's flask (v)	Alcohol added	Vol. of M/4.42 $CoCl_2$ reqd. (Titration curves (v_1)	Vol. of M/4.42 $CoCl_2$ calculated for 20 c.c. of M/48.65 K_4FeCy_6 $(20v_1/v)$	Eqv. Vol. of M/48.65 $CoCl_2$ $n(20v_1/v)$
20.0 c.c.	0.0 c.c.	2.20 c.c.	2.20 c.c.	24.4 c.c.
18.0	2.0	1.85	2.05	22.7 Curve No. 9
16.0	4.0	1.60	2.00	22.1 Curve No. 10
(ii) M/8.84 $CoCl_2$ and M/48.65 K_4FeCy_6. Conc. ratio = 1 :5.53				
2.00 c.c.	0.0 c.c.	4.20 c.c.	4.20 c.c.	23.2 c.c.
18.0 c.c.	2.0	3.60	4.00	22.1
16.0	4.0	3.10	3.88	21.5 Curve No. 11

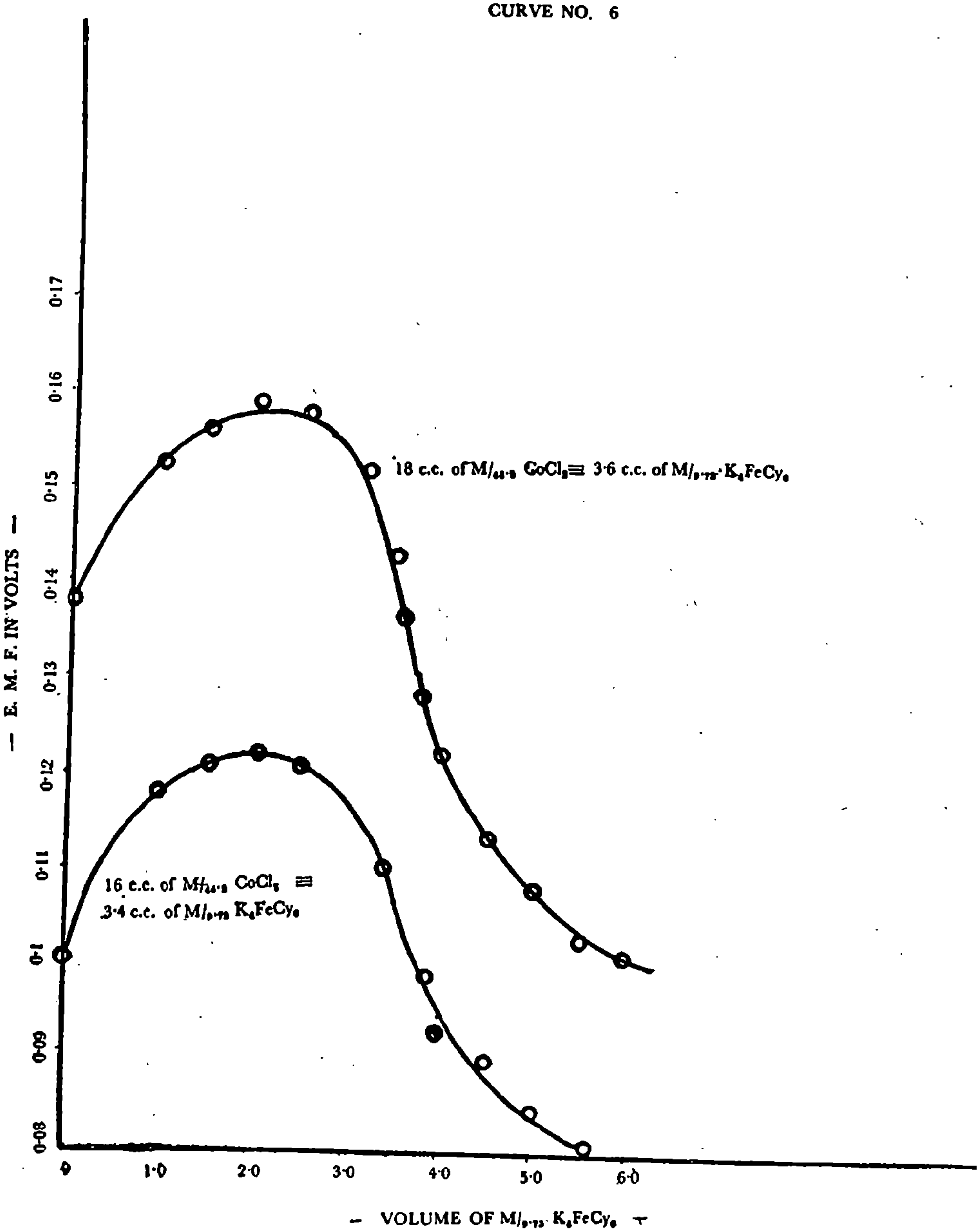


CURVE NO. 3

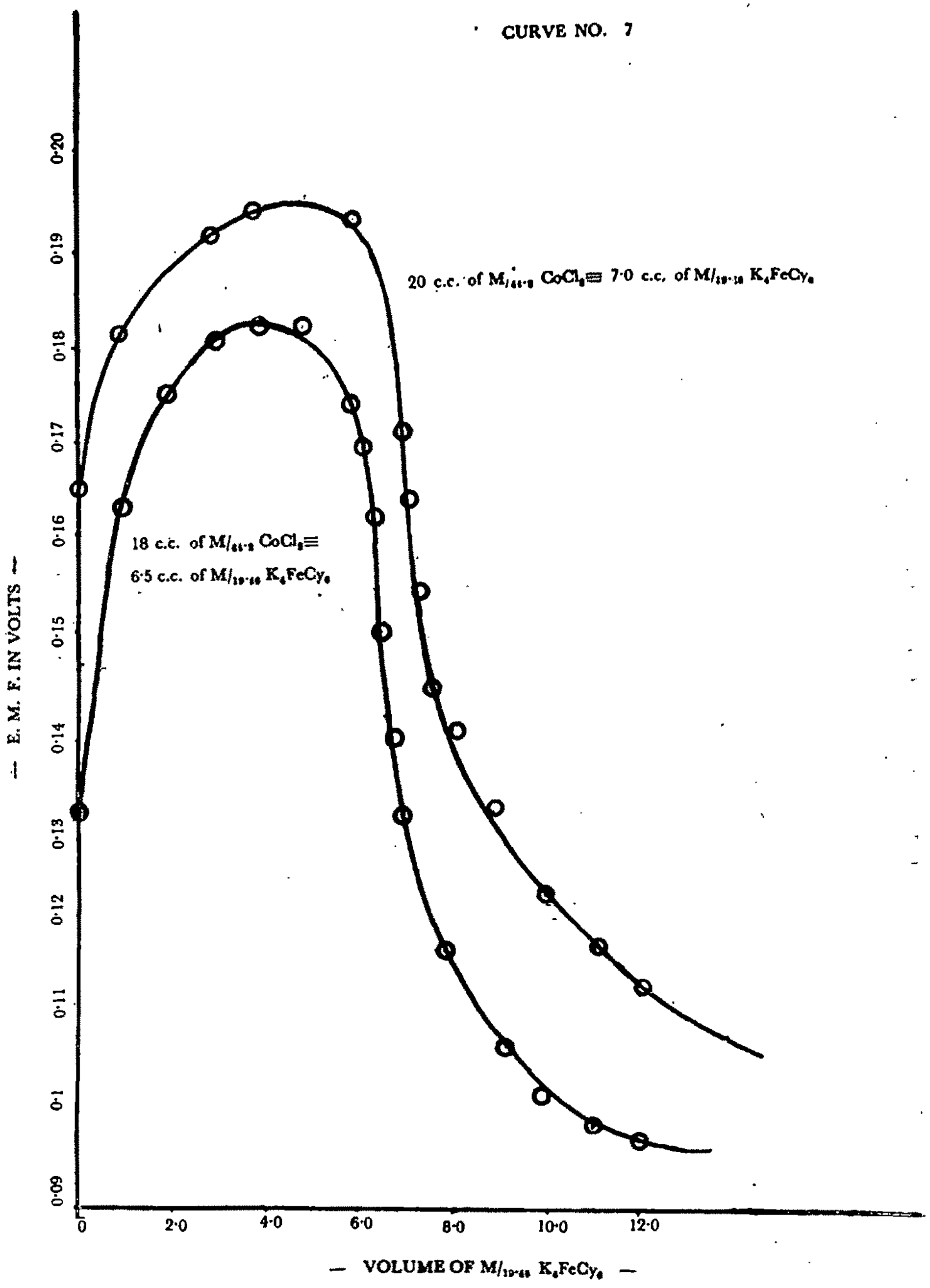
10 c.c. of $M/_{4\cdot 62}$ $CoCl_2$ ≡ ·85 c.c. of $M/_{4\cdot 885}$ K_4FeCy_6
18 c.c. of $M/_{44\cdot 3}$ $CoCl_2$ ≡ 83 c.c. of $M/_{4\cdot 885}$ K_4FeCy_6
8 c.c. of $M/_{44\cdot 3}$ $CoCl_2$ ≡ 80 c.c. of $M/_{4\cdot 885}$ K_4FeCy_6
— CONDUCTANCE × 10^3 MHOS —
32·0
30·0
28.0
26·0
24·0
22.0
20·0
18·0
16·0
14·0
12·0
10·0
8·0
0
0·25
0·5
0·75
1·0
1·25
1·5
— VOLUME OF $M/_{4\cdot 885}$ K_4FeCy_6 —


— E. M. F. IN VOLTS —
0·1
0·2
0·3
2·4
2·5
2·6
2·7
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
— VOLUME OF $M/_{9 \cdot 73}$ K_4FeCy_6 —
20 c.c. of $M/_{44 \cdot 8}$ $CoCl_2$ ≡ 3·5 c.c. of $M/_{9 \cdot 73}$ K_4FeCy_6
CURVE NO. 5

CURVE NO. 6


— E. M. F. IN VOLTS —
0·17
0·16
0·15
0·14
0·13
0·12
0·11
0·1
0·09
0·08
18 c.c. of $M/_{44\cdot8}$ $CoCl_2$ ≡ 3·6 c.c. of $M/_{9\cdot75}$ K_4FeCy_6
16 c.c. of $M/_{44\cdot8}$ $CoCl_2$ ≡ 3·4 c.c. of $M/_{9\cdot75}$ K_4FeCy_6
0
1·0
2·0
3·0
4·0
5·0
6·0
— VOLUME OF $M/_{9\cdot75}$ K_4FeCy_6 —

CURVE NO. 7


20 c.c. of $M/_{44\cdot8}$ $CoCl_2$ ≡ 7·0 c.c. of $M/_{19\cdot18}$ K_4FeCy_6
18 c.c. of $M/_{44\cdot8}$ $CoCl_2$ ≡
6·5 c.c. of $M/_{19\cdot18}$ K_4FeCy_6
— E. M. F. IN VOLTS —
0·09
0·1
0·11
0·12
0·13
0·14
0·15
0·16
0·17
0·18
0·19
0·20
0
2·0
4·0
6·0
8·0
10·0
12·0
— VOLUME OF $M/_{19\cdot18}$ K_4FeCy_6 —

CURVE NO. 8

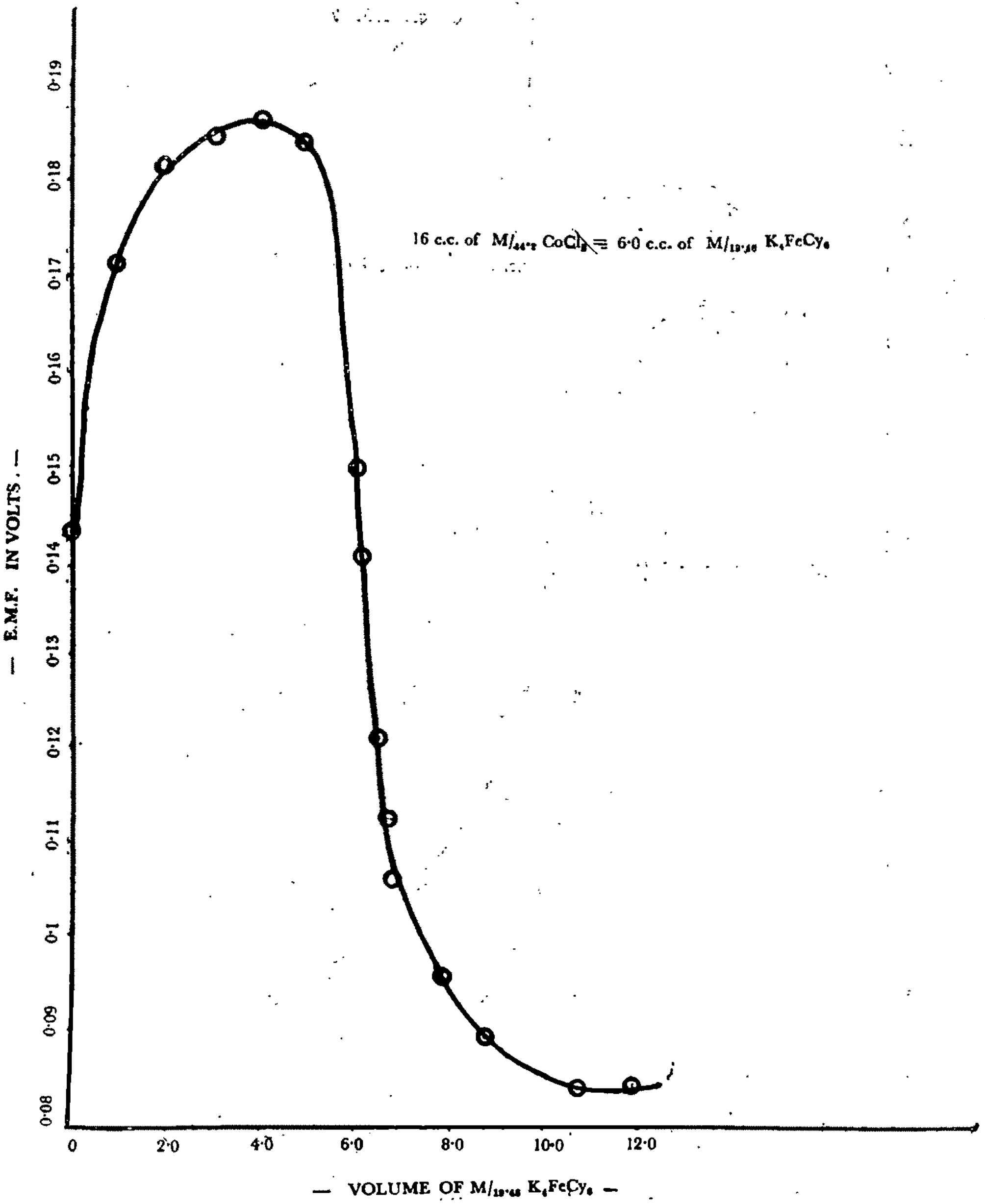

16 c.c. of $M/_{44\cdot8}$ $CoCl_2$ ≡ 6·0 c.c. of $M/_{19\cdot48}$ K_4FeCy_6
— E.M.F. IN VOLTS. —
0·08
0·09
0·1
0·11
0·12
0·13
0·14
0·15
0·16
0·17
0·18
0·19
0
2·0
4·0
6·0
8·0
10·0
12·0
— VOLUME OF $M/_{19\cdot48}$ K_4FeCy_6 —

TABLE V

Reverse thermometric titrations

(i) M/4.865 K_4FeCy_6 and M/44.2 $CoCl_2$. Conc. ratio (n) = 1 :9.07

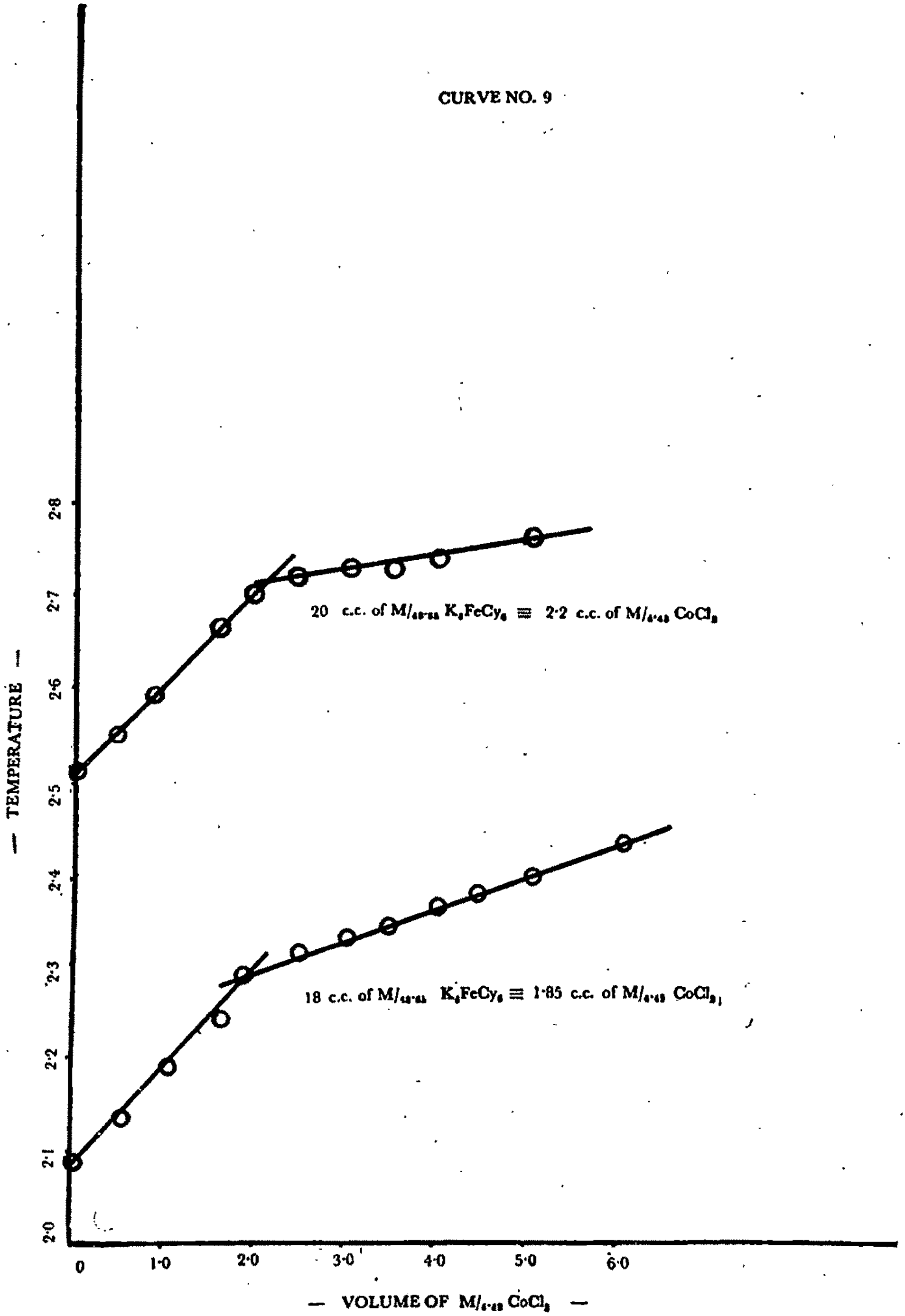
Vol. of M/44.2 $CoCl_2$ in Dewar's flask (v)	Alcohol added	Vol. of M/4.865 K_4FeCy_6 reqd. (Titration curves) (v_1)	Vol. of M/4.865 K_4FeCy_6 calculated for 20 c.c. M/44.2 $CoCl_2$ 20 (v_1/v)	Eqv. Vol. of M/44.2 K_4FeCy_6 n(20v_1/v)
20.0 c.c.	0.0 c.c.	1.70 c.c.	1.70 c.c.	15.4 c.c.
18.0	2.0	1.60 c.c.	1.77	16.0
				Curve No. 12
16.0	4.0	1.60 c.c.	1.77	16.0
(ii) M/9.73 K_4FeCy_6 and M/44.2 $CoCl_2$ Conc. ratio (n) = 1 :4.53				
20.0 c.c.	0.0. c.c:	3.50 c.c.	3.50 c.c.	15.9 c.c.
				Curve No. 13
18.0	2.0	3.24	3.44	16.3
16.0	4.0	3.20	4.0	18.1

DISCUSSION

The summarised results of the conductometric titrations of cobalt chloride with potassium ferrocyanide (carried out both in the direct and reverse order) throw much light on the composition and nature of the freshly precipitated cobalt ferrocyanide (vide Tables I and II; curves 1 to 4).

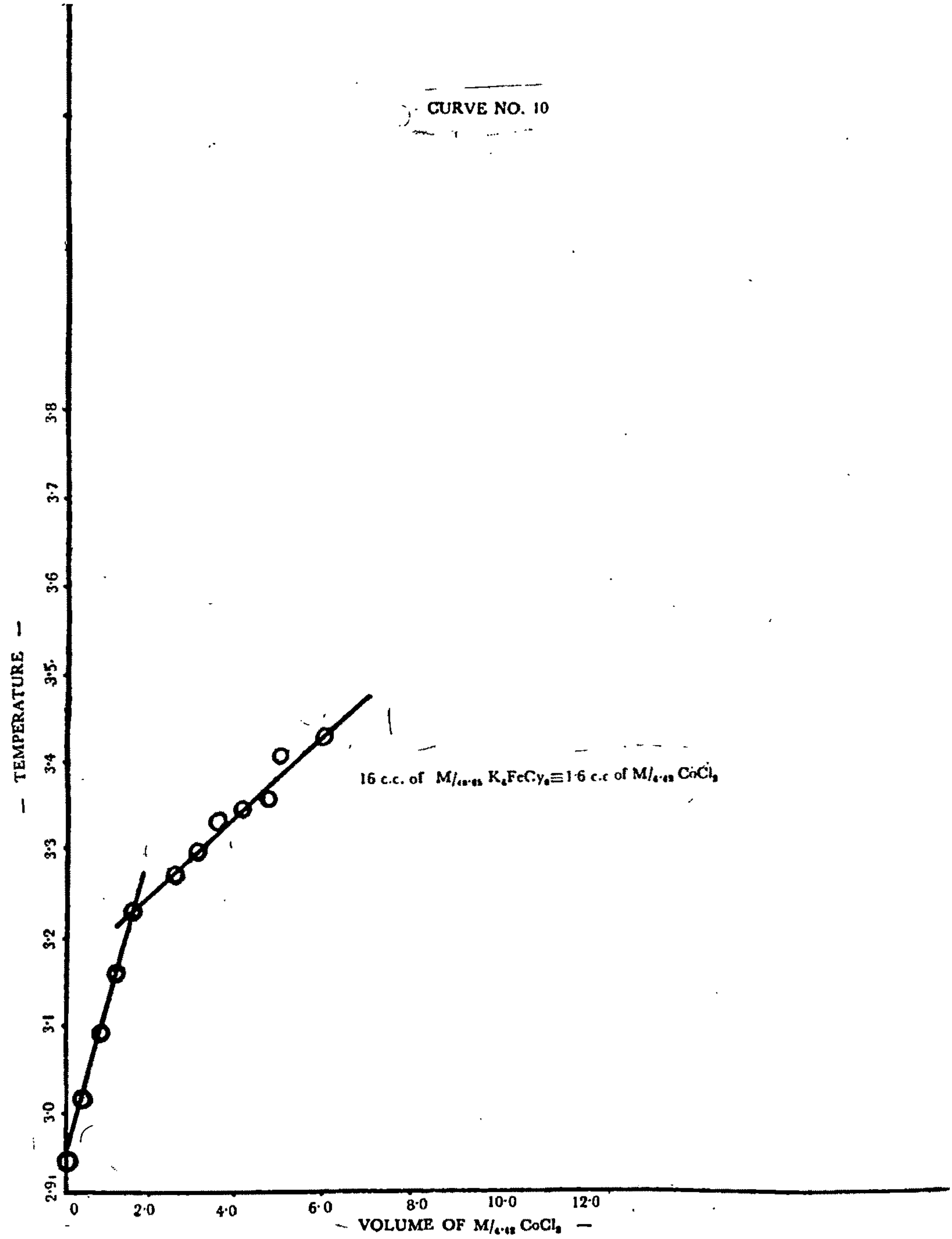
Interaction between $CoCl_2$ and K_4FeCy_6 can lead to the formation of such simple compounds as $K_2CoFeCy_6$; $CoFeCy_6$ and K_2Co_3 $(FeCy_6)_2$. 10.0c.c. of M/4·865 $K_4Fe(CN)6$ would need 10.0 c.c., 20.0 c.c., and 15.0 c.c. of M/4 .865 $CoCl_2$ (or, 19.0 c.c., 18.0 c.c., and 13.5 c.c. of M/4.42 $CoCl_2$—the concentration of $CoCl_2$ actually used in the titrations) for the formation of $K_2CoFeCy_6$; Co_2FeCy_6 and $K_2Co_3Fe(Cy_6)_2$ respectively in direct titration. Theoretical titre values for 10 c.c. of M/4.42 $Cocl_2$ in the reverse titration would be 10.0c.c., 5.0 c.c. and 6.6. c.c. of M/4.42 K_4FeCy_6 (or, 11.1 c.c.; 5.5 c.c. and 7.4 c.c. of M/4. 865 K_4FeCy_6—the concentration of K_4FeCy_6 actually used in the titrations).

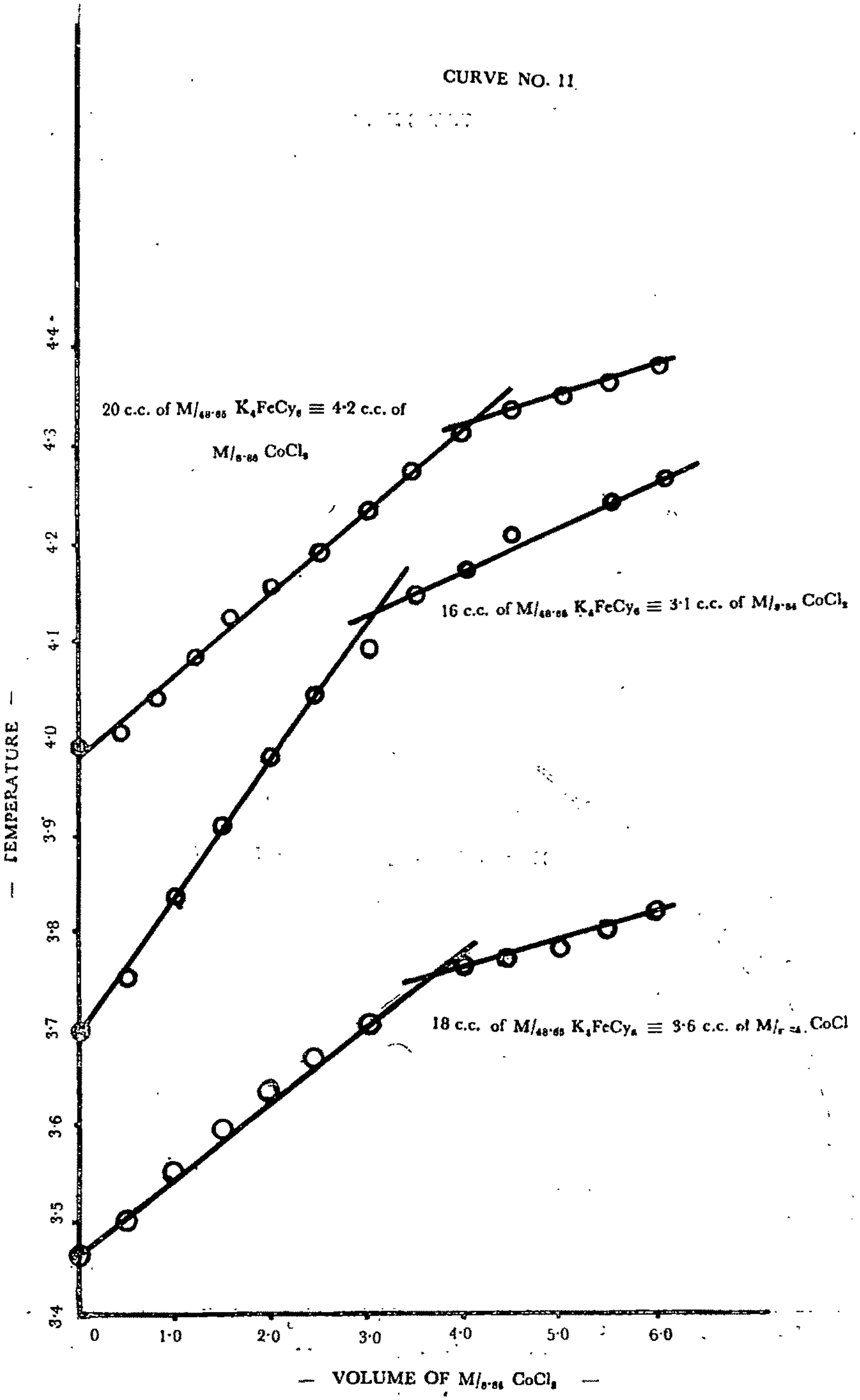
The observed titre values for 10 c.c. of K_4FeCy_6 solutions in aqueous medium is 12.1 to 12.2 c.c. of cobalt chloride solution, which, in presence of increasing amounts of alcohol decreases to 11.0 c.c. (vide table I). This is nearer to the theoretical value (10.0 c.c.) required for the formulation of the compound $K_2CoFeCy_6$. The change in the titre values by increasing the proportion of alcohol in potassium ferrocyanide solution suggests that the interaction between $CoCl_2$ and K_4FeCy_6 is influenced by such factors like adsorption effects and hydrolysis of cobalt ferrocyanide complex. However, this change can be best explained by the hydrolysing character of cobalt ferrocyanide (vide Part II of this paper). In aqueous solutions the precipitated cobalt ferrocyanide partially hydrolyses releasing free ferrocyanogen ions which will react with cobalt chloride added from the burette. As the quantity of alcohol is increased, the hydrolysis



CURVE NO. 9

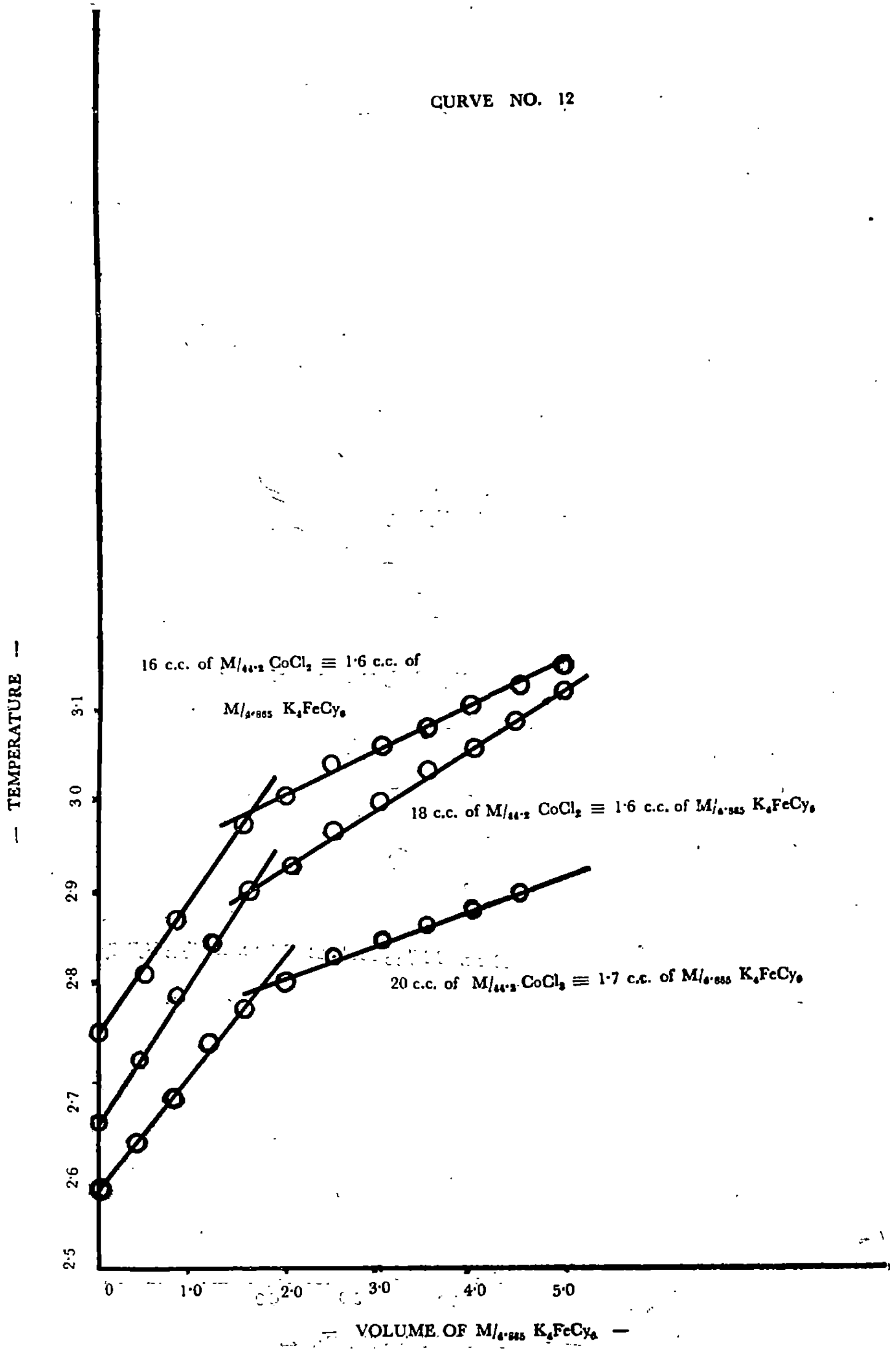
— TEMPERATURE —
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·8
0
1·0
2·0
3·0
4·0
5·0
6·0
— VOLUME OF $M/_{[illegible]}$ $CoCl_2$ —
20 c.c. of $M/_{[illegible]}$ K_4FeCy_6 ≡ 2·2 c.c. of $M/_{[illegible]}$ $CoCl_2$
18 c.c. of $M/_{[illegible]}$ K_4FeCy_6 ≡ 1·85 c.c. of $M/_{[illegible]}$ $CoCl_2$

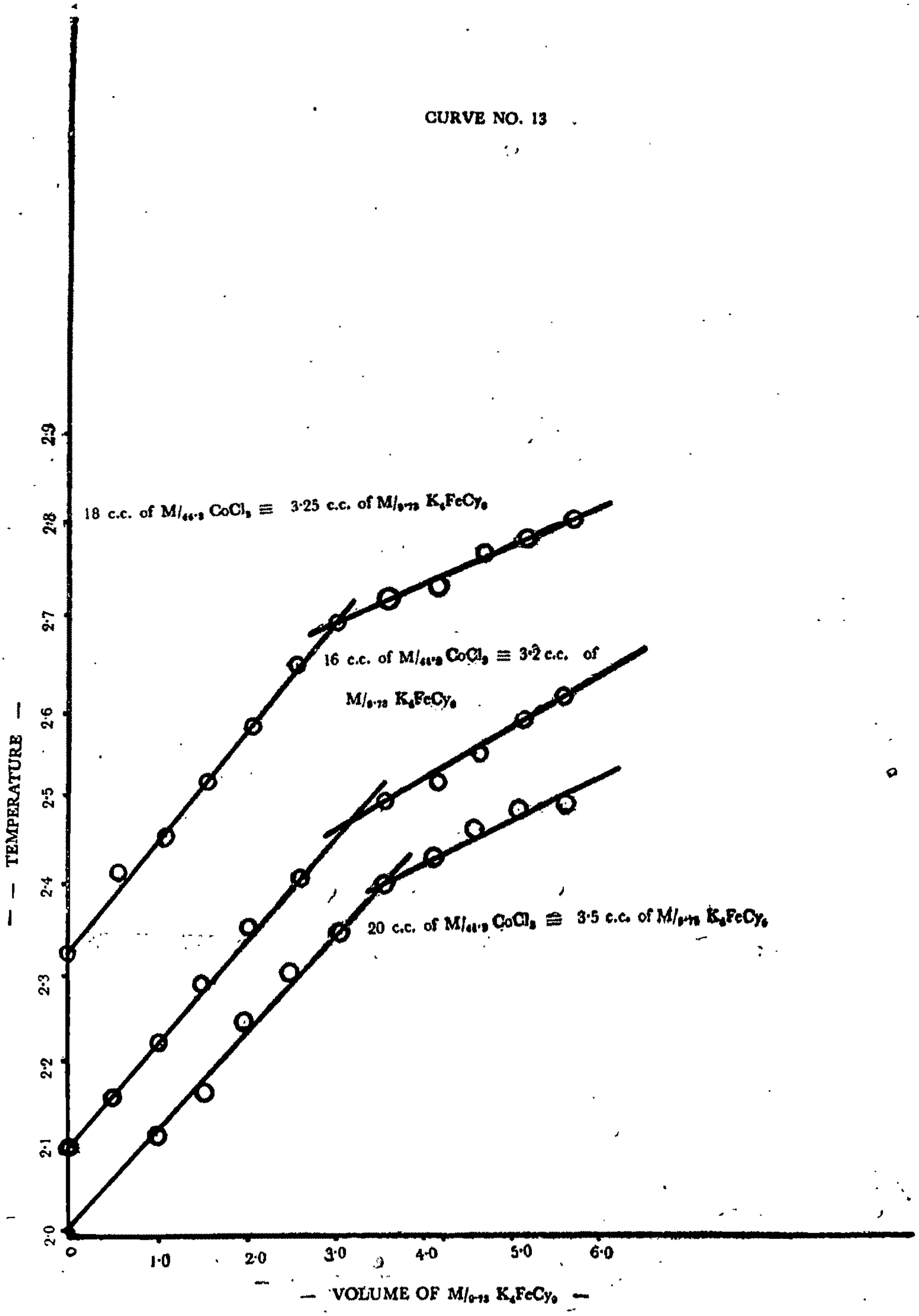

CURVE NO. 10
16 c.c. of M/[illegible] K_4FeCy_6 ≡ 1·6 c.c of M/[illegible] $CoCl_2$
— TEMPERATURE —
2·91
3·0
3·1
3·2
3·3
3·4
3·5
3·6
3·7
3·8
0
2·0
4·0
6·0
8·0
10·0
12·0
— VOLUME OF M/[illegible] $CoCl_2$ —



CURVE NO. 11

20 c.c. of $M/_{48\cdot65}$ K_4FeCy_6 ≡ 4·2 c.c. of $M/_{8\cdot84}$ $CoCl_2$
16 c.c. of $M/_{48\cdot65}$ K_4FeCy_6 ≡ 3·1 c.c. of $M/_{8\cdot84}$ $CoCl_2$
18 c.c. of $M/_{48\cdot65}$ K_4FeCy_6 ≡ 3·6 c.c. of $M/_{8\cdot84}$ CoCl
— TEMPERATURE —
3·4
3·5
3·6
3·7
3·8
3·9
4·0
4·1
4·2
4·3
4·4
0
1·0
2·0
3·0
4·0
5·0
6·0
— VOLUME OF $M/_{8\cdot84}$ $CoCl_2$ —


CURVE NO. 12
16 c.c. of $M/_{44\cdot2}$ $CoCl_2$ ≡ 1·6 c.c. of $M/_{4\cdot885}$ K_4FeCy_6
18 c.c. of $M/_{44\cdot2}$ $CoCl_2$ ≡ 1·6 c.c. of $M/_{4\cdot885}$ K_4FeCy_6
20 c.c. of $M/_{44\cdot2}$ $CoCl_2$ ≡ 1·7 c.c. of $M/_{4\cdot885}$ K_4FeCy_6
— TEMPERATURE —
2·5
2·6
2·7
2·8
2·9
3·0
3·1
0
1·0
2·0
3·0
4·0
5·0
— VOLUME OF $M/_{4\cdot885}$ K_4FeCy_6 —



CURVE NO. 13

18 c.c. of $M/_{44\cdot3}$ $CoCl_2$ ≡ 3·25 c.c. of $M/_{9\cdot73}$ K_4FeCy_6
16 c.c. of $M/_{44\cdot3}$ $CoCl_2$ ≡ 3·2 c.c. of $M/_{9\cdot73}$ K_4FeCy_6
20 c.c. of $M/_{44\cdot3}$ $CoCl_2$ ≡ 3·5 c.c. of $M/_{9\cdot73}$ K_4FeCy_6
— TEMPERATURE —
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·8
2·9
0
1·0
2·0
3·0
4·0
5·0
6·0
— VOLUME OF $M/_{9\cdot73}$ K_4FeCy_6 —

is more and more suppressed and hence the amount of $CoCl_2$ required for 10 c.c. of $K_4Fe(CN)_6$ in aqueous alcoholic medium becomes less and approaches the theoretical value.

The probable formula for cobalt ferrocyanide can be derived from the titration values when $CoCl_2$ is added to K_4FeCy_6. The calculated values of $CoCl_2$ required for 10 c.c. of aqueous K_4FeCy_6 when the reactants combine in the molecular ratio 1:1 and 3:2 are 10 c.c. and 15.0 c.c. respectively and hence 12.5 c.c. for the mixed complex. But the actual titre values for 10c.c. of K_4FeCy_6 are 12.1 and 12.2 c.c. (vide Table I), which agrees best with the value calculated above for the mixed complex. Hence the most probable formula for the cobalt ferrocyanide complex obtained by adding $CoCl_2$ to aqueous K_4FeCy_6 is $K_2CoFeCy_6$, $K_2Co_3\ (FeCy_6)_2$. The composition of the mixed compound changes in aqueous alcoholic medium towards the normal compound obtained by mixing $CoCl_2$ and K_4FeCy_6 in the molecular ratio of 1:1. It may, however, be argued that the composition of cobalt ferrocyanide is not a mixed compound but may have the molecular formula $K_4Co_4Fe(Cy_6)_2$ or it may be a double compound represented by the formula $2Co_2FeCy_6.K_4FeCy_6$.

In the case of titrations performed by reversing the order of mixing the solutions, it was found that the composition of cobalt ferrocyanide changes according to whether $CoCl_2$ is added to K_4FeCy_6 or vice versa. From the calculated values 10 c.c. of $CoCl_2$ require 10 c.c. of K_4FeCy_6 if they combine in the molecular ratio 1:1. But the observations from the titration curves show that 10 c.c. of $CoCl_2$ require 7.7 c.c. of K_4FeCy_6 when aqueous solutions are mixed together (vide Table II). In alcoholic solution, however, it is observed that the titre value of potassium ferrocyanide gradually increases to 9.0 c.c., that is, it approaches theoretical value (10 c.c.). The role of hydrolysis and adsorption effect on the precipitation of complex is in full agreement with the above observation. When $CoCl_2$ is taken in the titrating cell and K_4FeCy_6 is added from the burette, the precipitated cobalt ferrocyanide, on hydrolysis releases ferrocyanogen ions which, in turn, reacts with some $CoCl_2$ in the titrating cell. Hence, the amount of K_4FeCy_6 required for the point of equivalence must be less than the calculated amount and in alcoholic solutions, the amount of K_4FeCy_6 required would be more in consequence of the check of hydrolysis which is brought about by alcohol.

The probable formula of cobalt ferrocyanide complex when potassium ferrocyanide is added to cobalt chloride also points towards the formation of a mixed compound. The calculated values of K_4FeCy_6 required for 10 c.c. of aqueous $CoCl_2$ when the reactants combine in the molecular ratio 1:1 and 2:1 are 10 c.c and 5.0 c.c. respectively. Therefore, 10.0c.c. of aqueous $CoCl_2$ would require 7.5 c.c. of K_4FeCy_6 for the formation of the mixed compex $K_2CoFeCy_6$, Co_2FeCy_6. The actual observed titre value for 10 c.c. of $CoCl_2$ is 7.7 c.c which agrees with the value calculated for the mixed compound. Hence the probable formula for the cobalt ferrocyanide complex obtained by adding K_4FeCy_6 to $CoCl_2$ may be $K_2CoFeCy_6.Co_2FeCy_6$ or $K_2Co_3(FeCy_6)_2$.

Incidentally it may be noted that the latter compound was one of the components of the precipitated complex when $CoCl_2$ was added to K_4FeCy_6 taken in the cell.

Results obtained by conductometry are in agreement with those of the potentiometric and thermometric titrations (vide Tables III, IV and V).

Quantitative evidence on the hydrolytic and adsorptive behaviour of this complex follows in Part II of this paper.

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STUDIES ON THE DISEASES OF FOENICULUM VULGARE

2. Symptoms, morphology, phenological relations and the efficacy of the bordeaux mixture against *Cercospora foeniculi* Magn

By N. C. Joshi, *Botany Department, Government College, Ajmer.*

Introduction

While studying the parasitic fungi of Ajmer (Rajasthan) the writer came across two interesting diseases of *Foeniculum vulgare*, i. e. the powdery mildew and the blight in the year 1954. The former has already been described by Joshi (1957) in detail. The latter disease which is caused by the *Cercospora foeniculi* is also very serious in this district and now it appears in an epiphytotic form. This disease was first of all recorded by Sydow and McRae (1929) from Harwan, Kashmir and Pusa (Bihar). A preliminary account of this disease has been published from Ajmer in 1950, but the detailed studies are still lacking and the writer with the cooperation of Agriculture Department and some Agriculturists of Lotiana village has studied the symptoms, morphology of the fungus, phenological relations and the efficacy of the Bordeaux mixture against this disease.

Material and methods

Lotiana village where the plants were affected by the disease were visited thrice a week to study the symptoms. The infected portions, i.e. leaves, stem and fruits, were fixed in 70% Alcohol for the fungus study. Bordeaux mixture was used to see the efficacy against the disease. The phenological data was obtained from the Agriculture department Ajmer.

Symptoms

The disease was observed in the months of February and March 1954. The leaves, stem, peduncle and the fruits were mainly affected. At first the light brown spots were noticed on the leaves and later on the entire leaf turned dark brown. On the stem, branches and peduncle the spots were elongated and developed necrotic streaks. In severe cases the whole crop appeared as if it was burnt. The grains were either not formed and if formed they were shrivelled and blackened.

Morphology of the fungus

The sections of the diseased fruits, leaves and peduncle were cut and microscopic examination showed that the conidiophores were in groups of 6 to 8 and each conidiophore measured 53μ to $64\ \mu$ in length and 4μ to $6\ \mu$ in breath. The conidia were hyaline, sparsely septate and were borne at the tip of the conidiophores. The knee bends were conspicuous and prominent. The conidia got detached easily. The nature of conidia, conidiophore and their measurements of length and breath very much resemble with the description of *Cercospora foeniculi* Magn. given by Saccardo (1931).

PHENOLOGICAL RELATIONS OF THE BLIGHT

In order to arrive at some definite conclusions as to the relationship of the blight disease with the daily weather condition during the vegetative period of *Foeniculum vulgare*, it was observed that the atmospheric temperature exerts a great influence on the development of the blight disease. The parasite grows rapidly and produces abundant conidia. It was found that in the month of March, 1955 and 1956 when the disease was at its peak the maximum temperature on the majority of the days did not fall below 78° F. The average rainfall in this month was .52 inches in 1955 and .46 inches in 1956. It is clear from the table No. 1 that the slight warmer temperature (78- 95° F.) with some rainfall (.4 to .5 inches) caused the blight to become an epiphytotic resulting in a serious damage to the crop during 1955 and 1956.

Table 1

Showing the frequency of favourable and unfavourable temperature for the blight disease.

Year	Nuber of days in each month with favourable and unfavourble temperature indicated					
	Temperature below 78° F. (Unfavourable)			Temperature between 78-95° F. (favourable)		
	Jan.	Feb.	March	Jan.	Feb.	March.
1955	31 days	4 days	nil	nil	24 days	31 days.
1956	28 days	6 days	2 days	3 days	22 days	29 days.

Rainfall—January, .27 inches; February, nil; March, .52 inches (1955).
Rainfall—January, .1 inches; February, .15 inches; March, .46 inches (1956).

EFFICACY OF BOREAUX MIXTURE AGAINST THE DISEASE

In order to see wheather there is any affect of Bordeaux mixture against the disease, two plots were taken at Lotiana village for this purpose. Four applications of Bordeaux mixture were done, first in the month of January, the second in the month of February, the third in the month of March and the last in the month of April in 1955. The experiments were repeated in the year 1956. It was noted that the blight was present in a very low percentage in the experimental plots while in the control plots appreciable number of plants were affected by the disease as shown in table No. 2

Table 2

Showing the affect of Bordex mixture on blight disease of *Foeniculum vulgare.*

Year	Time of spraying	Treated plants (Experimental)				Untreated plants (Contraol)			
		Total No. of plants	No. of plants infected.	% of Infection	Average % of Infection	Total No. of plants	No. of plants infected	% of Infection	Average % of Infection
1955	Jan. 12	225	ni	0%	1·2%	280	nil	0%	37.5%
	Feb. 20	220	2	.9%		278	80	28.9%	
	March13	208	4	1.9%		270	160	58.6%	
	April 20	208	5	2%		263	165	62.8%	
1956	Jan. 10	180	nil	0%	0.9%	186	2	1.1%	23.5%
	Feb. .8	178	1	.5%		183	22	11.9%	
	March 6	176	2	1.1%		174	50	28.7%	
	April 13	175	4	2.2%		165	86	52.4%	

It will be observed from the table No. 2 that the disease can be controlled appreciably by spraying the plants with Bordeaux mixture at intervals, i.e., January, February, March and April.

SUMMARY

A blight disease of *Foeniculum vulgare* caused by *Cercospora foeniculi* Magn. has been reported from Ajmer.

The symptoms of the disease, morpohlogy of the fungus, phenological relations and the efficacy of the Bordeaux mixture against the blight have been described.

ACKNOWLEDGEMENT

I am grateful to Shri B. R. Sharma, an Agriculturist of Lotiana village for this help in setting up some experiments in his fields. My thanks are due to Agriculture department for supplying the phenological date. I am also thankful to Principal Bhim Sen and Prof. B. Tiagi for Lab. Facilities.

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ENTOMOLOGICAL SURVEY OF THE HIMALAYA*

PART XIX.—FAUNISTICS OF HIGH ALTITUDE COLEOPTERA FROM THE NORTH-WEST HIMALAYA.

By M. S. MANI and SANTOKH SINGH, *School of Entomology, St. John's College, Agra.*

I. INTRODUCTION

An attempt is made in this paper to summarize the available information on the faunistics of the high altitude Coleoptera from the North-West Himalaya. Though these insects have been collected from the region for over half a century, a properly planned faunistic survey does not seem to have been made and our knowledge of the high altitude Coleoptera of the North-West Himalaya must remain largely incomplete for a long time to come. The earliest collections of Coleoptera from this part of the world were perhaps made Hügel and by the Yarkand Mission[1] in 1878. Babault, the celebrated French naturalist, who travelled through Kangra, Kulu and Lahaul Valleys and through Ladak and parts of Kashmir in 1914, brought back a farily large collection of beetles among other insects.[2] In recent years the Yale University North India Expedition and the Zoological Survey of India have collected, chiefly from Kashmir. Three Entomological Expeditions from the School of Entomology, St. John's College, Agra, have been studying the high altitude insects from the region and have brought back large collections of Coleoptera.

We know at present about 700 species of Coleoptera (distributed over 23 families), representing nearly a third of the total insect fauna of the North-West Himalaya as a whole.[3] Considering the extreme conditions of life above the timber line[4], this number would appear suprisingly large; recent experience of the Entomological Expeditions has however shown that a very large number of species of Coleoptera still await discovery. While considerable attention seems to have been paid to certain families, others appear to have been comparatively neglected. Collections have been made from a great variety of altitudes and localities (*vide* map in fig.1), clustered along the periphery roughly of a wide circle. A large central area, comprising the Zaskar and Ladak Ranges, still remains wholly unexplored in so far as the insect life is concerned. While the eastern and central Himalayas have been relatively more thoroughly surveyed, the North-West Himalaya has been very much neglected. Inspite of the comparative incompleteness, the available data are in no sense inaccurate in themselves, except only as estimates of those of larger samples from a more thorough survey in future, and may be taken as a fairly good random sampling of the Coleoptera of the North-West Himalaya. Analysis of the material is bound to indicate the more general features of the high altitude Coleoptera and should perhaps lead to further detailed investigations.

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*Contribution No. 72 from the School of Entomology.

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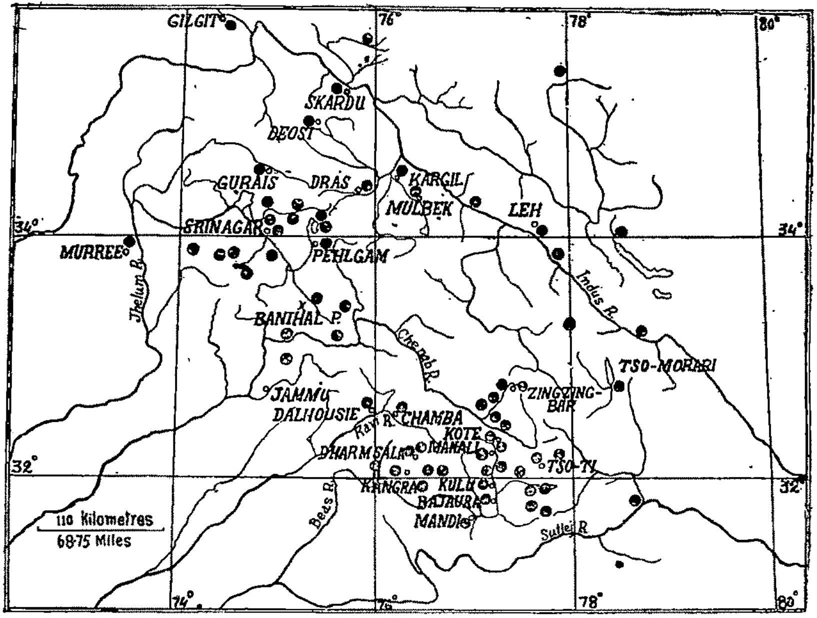

Fig. 1. A sketch map of the North-West Himalaya, showing the area of Coleoptera survey. Small black circles indicate approximately the localities. For the sake of simplicity the mountains are not shown.

All the species so far known from the region were tabulated in the form of frequency distribtution of random samples, percentages rather than actual numbers being considered in each case. Standard deviations of the percentages were calculated according to the formula

$$6=\sqrt{N.\ p.\ q.}$$

where *6* is standard deviation, N the total number of species, *p* the probability of the species occurring and *q* the probability of its not occurring, expressed as decimal fractions. The sampling limits were in each case calculated as for small faunal samples according to the formula $Np-3\sqrt{N.p.q.}$ for the lower limits and $Np+3\sqrt{N.p.q.}$ for the upper limits, where N is the size of the actual sample (the number of species so far known) and $3\sqrt{N.p.q.}$ is 3 times the standard deviation. In the study of the relation between the abundance of species and altitude, the primary object was species occurring above the timber-line. For purposes of comparison, the species occurring immediately below were also taken into cconsideration. The species were grouped into three broad groups according to the altitude of occurrence. The first group is from the first zone of moderate altitudes between 6000 ft. and 10,000 ft. above mean sea level. The second zone is a transitional belt near the tree-growth limits, 12,000 ft. on the outer and 10,000 ft. on the inner ranges and sometimes even lower than 10,000 further north. The third zone comprises the extreme high altitudes beyond the limits of three-growth and reaching nearly up to 20,000 ft. and above in the North-West Himalaya. While the boundaries between the first and the second zones are not sharp, the third is however distinctly marked off from the others. The abundance of species of the various families in the zone was measured with reference to the total Coleoptera of the zone and the total species of the family in the region.

$$\text{Zonal index} = \frac{\text{Number of species of the family in the zone} \times 100}{\text{Total number of species of all families within the zone.}}$$

$$\text{Family index} = \frac{\text{Number of species of the family in the zone} \times 100}{\text{Total number of species of the family in the North-West Himalaya}}$$

In addition to the study of the influence of altitude on the occurrence and abundance of Coleoptera, the effect of the differences of the aspects of the mountain ranges were also investigated. In the analysis of the horizontal distribution of species an attempt has been made to determine the proportion of various zoogeographical elements.

II. GENERAL OBSERVATIONS

The peculiarities of the Coleoptera of the North-West Himalaya are due to the combined effects partly of altitude and partly of the higher latitude of the region. The North-West Himalaya lies between 31° and 36° North Latitude, while the greater part of the rest of the Himalaya is contained within the limits of 27° and 29° North Latitude. Except for small areas in Kashmir no place in the region is on the whole below an elevation of about 10,000 ft. above mean sea level, thus largely above the timber-line. We have already published a brief account (*loc. cit.*) of the general features and the special ecological conditions of life in the North-West Himalaya.

As in nearly all other Orders of insects, among the Coleoptera also there is a general sparseness of variety. We see on the whole localised concentrations of large numbers of individuals of comparatively few species in each family. Not only is the proportion of species in the different families less than in the plains, but the actual density of population of species is also very much less than on the plains. The distribution of species in the different families is summarized in table IV. Thirteen out of the 23 families,viz. Dytiscidae, Gyrinidae, Paussidae, Hydrophilidae, Rhysodidae, Nitidulidae, Erotelidae, Endomychidae, Coccinellidae, Meloidae, Dynastidae, Cerambycidae, and Chrysoymelidae are extremely sparse and their combined total does not amount to 25% of the total number of species of Coleoptera from the region. Carabidae, Staphylinidae and Curculionidae are, the most abundant, both as species and as individuals and the first two families also occur at much higher elevations than the rest of Coleoptera. The species of Carabidae represent about 36.5% of the total Coleoptera of the region; the figure for Staphylinidae is 20.5%. Out of each random collection of 100 species of Coleoptera from the region, not less than 32 species will on the average belong to Carabidae and 16 to Staphylinidae. The sampling limits for most of the remaining families are hardly about 1, so that in any random faunal sampling of the North-West Himalaya we may never come across even a single species of the great bulk of these families. The combined strength of Carabidae and Stephylinidae is somewhat more than that of the remaining families, both as species and as individuals.

We know about 1500 species of Carabidae from the faunal region of India and about 200 of these are found in the North-West Himalaya. The species occur mostly under stones in the neighbourhood of the glacial torrential streams, edges of snow fields, high altitude lakes and other damp or moist localities on alpine meadows. Although the subfamily Trechinae is often cavernicolous, none of the species so far known from the region have been found in caves. The relatively long and slender legs, which the Cicindelidae have as adaptation for fast running, seem to be quite unsuited on the wind-blown, hard and exposed rock or snow. The family Staphylinidae, the second in importance, inhabits a wide variety of habitats like moss, organic debris under stones near the edges of snow fields, ants' nests, etc. A species of *Atheta* is common on snow fields. A number of species have been found in cavities near the edges of terrential streams or in damp areas. Coccinellidae include almost exclusively carnivorous types. Though fairly abundant in other parts of the Himalaya, the family Sacarabaeidae is relatively very poorly represented in the North-West Himalaya.

There is a general preponderance of flightless and subterranean types, which are also mostly either active predators, carrion feeders or scavengers. In the generally treeless, cold, dry and wind-blown elevated regions of the North-West Himalaya, forest and aquatic forms as well as phytophagous species are either extremely rare or wholly non-existent. The surface-haunting aquatic species are entirely restricted to relatively low elevations and that also mostly to the outer ranges.

In heavy localised concentrations of individuals in favourable micro-climatic niches, associations of Carabidae, Tenebrionidae, Acarina, Chilopoda and Dermaptera are common. Mass assemblages of Coccinellidae and large swarms of a single species of Meloidae, *Mylabris phalerata*, have been met with up to nearly 14,000 ft. above mean sea level on some of the outer ranges.

The Bembidine Carabidae of the tribe Anillini are among the smallest beetles and measure about 1-2 mm. long. They are flightless and have greatly reduced or atrophied eyes. The species occur mostly under deeply sunk boulders or fissures in damp soil on alpine meadows. They penetrate deeper in winter, but move near the surface during summer, when the snow melts. Being found under stones, the antennae, palpi and legs are generally short. The Trechini are also usually found in alpine meadows, edges of snow fields, beneath moss, stones, etc. Several of the species are flightless, with more or less reduced wings. The family Carabidae is represented mostly by species of *Bembidion*, a genus of temperate regions, with only one or two species occurring in the plains in India. Half the total number of species of *Bembidion* so far known from India inhabit the North-West Himalaya. *Philonthus*, *Atheta*, *Oxypoda* and *Tachinus* are the common Staphylinids of the North-West Himalaya.

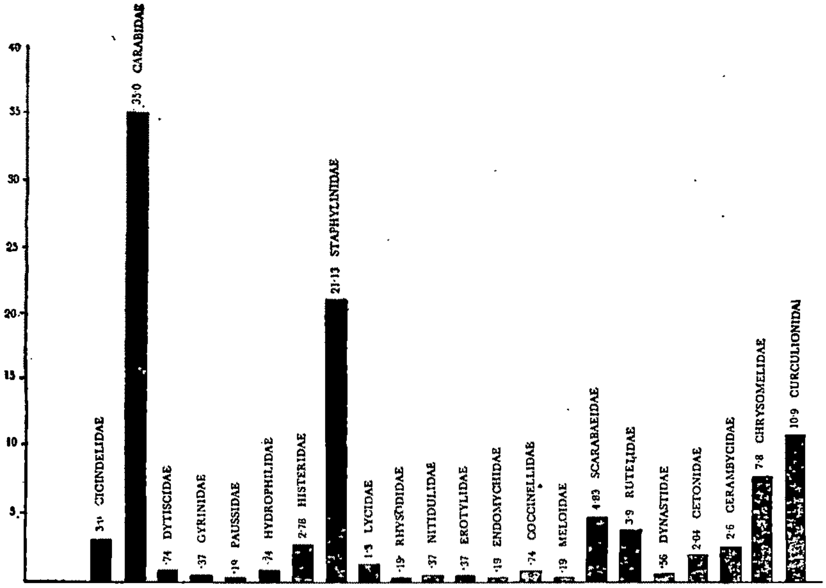

Fig. 2 The zonal indices of families from the first zone in the North-West Himalaya,

III. Altitude and Distribution

There is very close relation between the altiutude and distribution of species, its habits and local conditions. With the increase in altitude there is not only marked fall in numbers of families, genera and species, but an extremely interesting succession of types—a succession characterised by more or less pronounced replacement of forms characteristic of a given altitude by others. Some of the families disappear entirely above comparatively low elevations. Above 6000 ft. for every increase of about 2000 ft. altitude, the number of species is roughly halved up to nearly the timber-line, beyond which the fall is abrupt and more than three times as before.

Due to the higher latitude, differences in the general trend line of the ranges, greater aridity, higher permanent snow line and much greater width of the North-West Himalaya, comparatively fewer species reach extreme altitudes. No Coleoptera seems to have been taken so far beyond an elevation of 17,000 ft. in the region. The maximum altitude record for the Order in the North-West Himalaya is in the family Carabidae, with Staphylinidae coming next (table III). The families Cicindelidae, Histeridae, Curculionidae, Scarabaeidae and Cerambycidae have not been found above 12,000 ft. The highest altitude at which Chrysomelidae have been taken is 15,000 ft. The carabids *Amara brucei* and *Bembidion nivicola* Andr. occur a little below 17,000 ft. both in the North-West Himalaya and near Mt. Everest in the east. In the North-West Himalaya Curculionidae have not so far been found beyond 14,000 ft., but at least one species *Catopionus semivittatus* Schwinh. occurs up to 16,000 ft. in the Teesta Valley in Eastern Himalaya. Erotylidae, Scarabaeidae, Rutelidae and Chrysomelidae have not been found above 9000 ft., 11,000 ft. and 15,000 ft. respectively in the North-West Himalaya, but in other parts of the Himalaya the maximum altitude records for these families are 11,000 ft. 13,000 ft., 13,000 ft. and 16,500 ft. respectively. In the case of Staphylinidae the maximum altitude is 16,000 ft. in the North-West Himalaya and Garhwal-Kumaon Himalaya. *Atheta* (*Microdota*) *ladakiana* Cam. occurs at 16,000 ft. in the North-West Himalaya and *Atheta* (*Paraloconota*) *dissociata* was reported at 15,750 ft. in Kumaon. *Geodromicus brevitarsus* was also found in the same locality at the same altitude, but in the North-West Himalaya the genus does not seem to occur above 8000 ft.

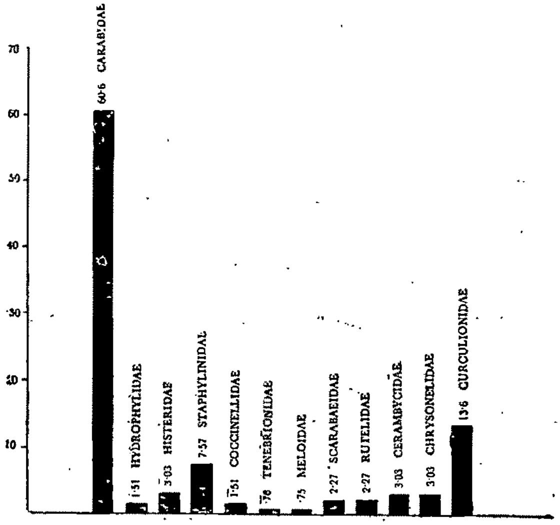

Fig. 3. Zonal indices of families from the second zone in the North-West Himalaya

First zone.—The great bulk of species so far known from the region occurs within the limits of this zone. A total of 540 species, representing nearly 92% of the Coleoptera fauna of the North-West Himalaya, has been recorded (table IV, fig. 2). The species are largely tropical or temperate forest types and some of them also occur in the plains. The zone thus seems to represent the meeting point of the tropical and high altitude elements. In most families nearly 97% of the species known from the region would appear to belong to this zone. About 35% of the Coleoptera occurring within the zone belongs to the family Carabidae. Staphylinidae, which stands second in importance, has a zonal index of 21.13%, with Curculionidae standing third in order of abundance of species (zonal index 10%). *Bembidion* is the dominant genus. Other carabid genera like *Axonya*, *Brachinus*, *Coelosternus*, *Craspidonotus*, *Cyclosternus*, *Karya*, *Notiophilus*, *Omophron*, *Platymetopius*, *Sphodrus*, *Tachys* and *Tetragonoderus* seem to be confined to the first zone. About 80% of the species occurring in the zone are restricted to it; 17% occur in the first and second zones and 3% are common to the first and third zones (table VII).

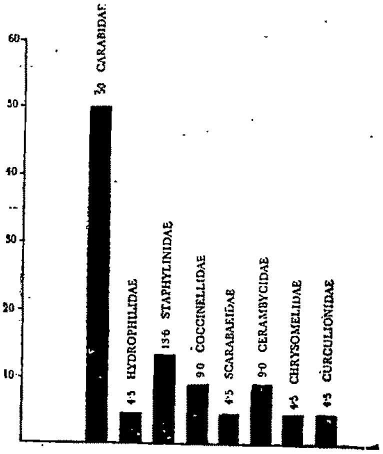

Fig. 4. The zonal indices of families from the third zone in the North-West Himalaya

Second zone.—With the replacement of forests by exposed and wind-blown alpine meadows in this zone, forest species give place mostly to endogeous, localised concentrations of scavengers and carnivorous forms. Altogether 132 species, distributed over 13 families, have so far been recorded within the limits of the transitional zone. A number of well known families like Cicindelidae, Dytiscidae, Gyrinidae, Paussidae, Lycidae, Rhysodidae, Nitidulidae, Endomychidae, Dynastidae and Cetonidae are often absent. Carabidae and Staphylinidae continue however to dominate. On an average about 27% of the total species of the North-West Himalaya in each family occurs in the transitional zone and in the case of Staphylinidae this figure is as low as 3%. Nearly 60% of the Coleoptera occurring here are Carabidae. The pronounced superiority of Carabidae may be readily seen from the histogram in fig. 3. Among the genera which are common may be mentioned *Bembidion*, *Hister*, *Atheta*, *Coccinella*, *Mylabris* and *Onthophagus*. About 66% of the species inhabiting this zone are often also to be met with in the upper reaches of the first zone (table VII, fig. 5). Only 23% of the species are strictly restricted to the zone. A comparatively small percentage (11%) of the transitional zone species represents incursions from higher elevations. Compared to the first zone, a conspicuous drop by about 4 times in the proportion of species, which are restricted to the zone, is observed. In table VIII is given the inter-zonal overlapping of the altitudinal distribution of Carabidae. About 67% of Carabidae from the transitional zone are common to it and the first zone, 24% restricted to the zone and 9% occur both here and in the third zone.

Third zone.—The third zone represents the extreme high altitudes beyond the timber-line. Extensive areas including even the higher valleys in Lahaul, Ladak, Zaskar and parts of Kashmir fall within this zone. Correlated Spiti, with the total absence of trees, forest types of Coleoptera are replaced by meadow-inhabiting species, which occur mostly underground, under stones and other similar sheltered situations. Naturally no arboreal species occur above the timber-line. Phytophagous species are mostly leaf-feeders near about 12,000 ft. but beyond 14,000 ft. are wholly root-feeding types. The plants are low-matted dwarfs with perennial underground roots and stems, which serve as the only source of food for phytophagous species of this zone. The zone is quite sharply marked off from the transitional belt.

An extremely small number of families, viz. Carabidae, Hydrophilidae Staphylinidae, Coccinellidae, Scarabaeidae, Cerambycidae, Chrysomelidae and Curculionidae, have successfully extended their range into this zone. Carabidae, Staphylinidae and Coccinellidae have in particular colonised much higher elevations than others and are also numerically far superior, both as species and as individuals in the third zone. The genera above the timber-line approximately constitute about one-third that found in the transitional belt and about one-twentieth that occurring below 10,000 ft. Of the dozen genera so far collected from the third zone, *Bembidion*, *Calosoma*, *Atheta*, *Coccinella* *Onthophagus* and *Scepticus* may perhaps be mentioned as the more important and commonly met with. *Bembidion* outnumbers all others in the number of species and has also been taken at great elevations. *Bembidion nivicola* has already been referred to as occurring nearly up to 17,000 ft. Two species of Staphylinidae viz. *Atheta* (*Bessobia*) *submetallica* and *Atheta* (*Microdota*) *ladakiana* have been collected at 16,000 ft., representing the highest altitude at which a Styaphylinid has so far been found in any part of the Himalaya. A third species *Atheta* (*Oreostibia*) *nimbicola* occurs at 13,000 ft. A single species of Chrysomelidae *Leptosonyx octocostatus* has been recorded at 15,000 ft.

Between 12,000 ft. and 14,000 ft. there are eight species of *Bembidion;* above 14,000 ft. there are also 8 species of the same genus. The family index with an average of 14.3 (vide table IV) is about half that of the transitional zone. The average zonal index has risen to 12.5 Almost 50% of the Coleoptera of this zone are Carabidae, and 13.6% are Staphylinidae. About 17% of the species of this zone are restricted to within its limits, 44% occur both here and in the transitional zone. The species which are characteristic of the first zone are rare here. Near the timber line the ranges of the lower altitude forms and those of the third zonal forms usually overlap, but in the upper reaches of the third zone none of the species from the lower elevations are ever found.

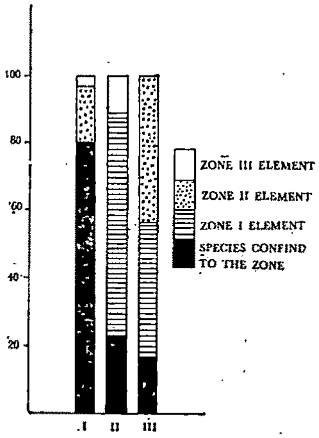

Fig. 5. Overlapping of the altitudinal of range distribution in the three zones of the North-West Himalaya. I, II and III represent zones of altitude.

Considering the species generally occurring above 6000 ft., we find that about 78% occur in the first zone, 19% in the second zone and 3% in the third zone. Out of every 50 species (table IX) collected at random from the North-West Himalaya, we may on the average get 35 from the first zone, at least 5 in the second zone and none at all in the third zone. Similar sampling limits for Carabidae are given in table X.

The influence of altitude on the distribution of Coleoptera is recognized not only in the fall in abundance with increase in the altitude, but an extremely interesting succession of genera and species is also seen. While a few genera and species occur from about 6000 ft. above mean sea level up to nearly 20,000 ft., numerous others disappear at various altitudes and their place is taken by newer types. In table V is presented the succession of genera of Carabidae at intervals of 2000 ft. from 6000 ft. upwards to nearly 17,000 ft. *Bembidion* and *Calosoma* have been found throughout from 6000 ft. to 14,000 ft. but only *Bembidion* occurs above 14,000 ft. *Hypsinophus*, *Liocnemis* and *Trichocellus* appear between 8000 ft. and 10,000 ft. and do not ascend to altitudes higher than 12,000 ft. Five genera *Chaetobroscus*, *Cymindis*, *Drypta*, *Dyschirius* and *Licinus* occur only between 10,000 ft. and 12,000 ft. The genus *Leistus* is confined to a narrow belt between 8000 ft. and 10,000 ft. As we rise above 8000 ft., 27 genera disappear, but 4 not found below occur for the first time. Two of the genera found commonly between 8000 ft. and 10,000 ft. are replaced by the five named above beyond 10,000 ft. The altitudinal succession of species of the typically high altitude carabid *Bembidion* at intervals of 2000 ft. (table VI), shows the replacement by *B. hutchinsoni* of *B. luntaka* above 14,000 ft.

IV. Aspect and Distribution

The occurrence, abundance and habits of the various species depend not simply on altitude, but the aspect of the mountain ranges often very greatly modify the affect of altitude. The altitudinal limits of life zones differ very considerably on southern and northern aspects. At approximately the same altitude the species complex is by no means the same on the southern and northern slopes.

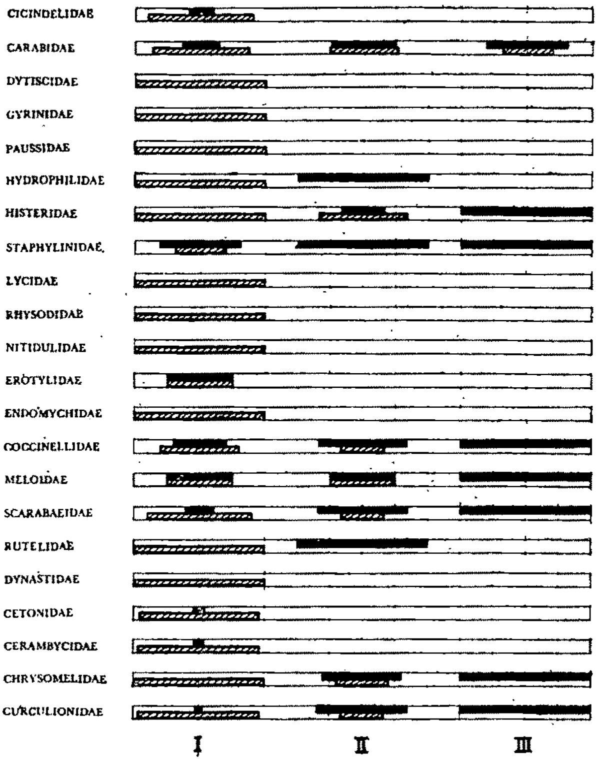

Fig. 6. Relation between aspect and abundance of species. Black bars indicate percentage abundance on north slope and striped bars on south slopes. I, II and III represent zones of altitude.

Taking the North-West Himalaya as a whole, the species of Coleoptera are nearly three times more abundant on the southern than on the northern slopes. Of remarkable interest is the fact that a number of well known families like Paussidae, Rhysodidae, Endomychidae, Dynastidae, Gyrinidae, Lycidae and Nitidulidae have not so far been recorded from the northern slopes in the North-West Himalaya. Among the Coleoptera so far collected, hardly 10 to 15% alone seem to occur simultaneously both on the north and south slopes. There is at higher elevations a general increase in the proportion of the northern slope species (table II, fig. 6). The family Staphylinidae seems somewhat exceptional in the much larger proportion of north slope species. In the first zone the northern aspect species of Carabidae constitute about 27% of the total zonal Carabids. In the second zone almost equal number of species occur on north and south and in the third zone more than 60% are on the northern aspect. The rise in the proportion of northern slope to the southern slope Coleoptera may be readily seen from table II. Below the timber-line the northern slope species represent only 13%, in the transitional zone 70% and in the third zone 95% respectively of the species occurring in each zone. There are practically no species of Staphylinidae on the southern aspect above 10,000 ft. In most families the northern aspect species are quite distinct from those of the southern slopes. The differences between northern and southern slopes appear to be greater in the North-West Himalaya than in the rest of the Himalaya. Taken as a whole, the differences between the northern and southern slopes Coleoptera seem to be due to a variety of differences of environmental factors, rather han to any single large factor. As most high altitude Coleoptera are endogeous, the various factors are to be traced to the soil temperature and moisture, which are ultimately dependent on the differences in the angle of incidence of the sunray. The southern aspect species appear to be largely comparatively recent invasions from lower elevations and the northern aspect types are undoubtedly older. The proportion of the northern slopes species seems to be larger than in the rest of Himalaya. As we pass from the Dhauladhar over the Great Pir Panjal, Great Himalaya, Zaskar and Ladakh Ranges, the typically southern aspect forms become less and less frequent. On the northern slopes certain species seem to occur at comparatively higher elevations than on the southern slopes, due perhaps to the higher snow line on the north.

Nearly 87% of the Coleoptea from the first zone occur on the southern slopes. Extremely rarely does a species occur both on the south and north slopes. The families Dytiscidae, Gyrinidae, Paussidae, Lycidae, Rhysoortae, Nititudlidae, Endomychidae and Dynastidae, so far recorded from below the timber-lime occur only on the southern slopes. Histeridae and Chrysomelidae, known only on the southern aspect in the first zone, occur both on the southern and northern aspects in the transitional zone. Hydrophidae, and Rutelidae, which are recorded exclusively on the southern slopes in the first zone, occur only on the northern slopes in the second zone. No species of Staphylinidae seems to have been collected from the southern slopes of this zone. In the case of Curculionidae, Scarabaeidae and Coccinellidae, we have nearly twice as many species on the southern slopes as on the northern. Hydrophilidae and Rutelidae appear on the northern aspect for the first time in the transitional zone. Histeridae differ from [all the other families occurring in this zone in its greater poroportion of southern forms. Nearly twice as many species occur on the southern slopes as on the northern. Both Histeridae and Chrysomelidae do not seem to have been found on the northern slopes in the first zone, but do so for the first time in the second zone. The latter family however predominates on the northern aspect as compared to the Histeridae. About 75% of the species occurring in the transitional zone have been collected on the northern slopes. This represents an increase of nearly 5 times over the first zone. The number of species occurring on the southern lopes is about one-third that in the first zone. It is interesting to note that the number of species of Carabidae from this zone found on the northern slopes is nearly equal to that recorded from the southern slopes.

In the third zone, except Carabidae, no other Coleoptera seem to have been collected on the southern aspect. This family occurs on the northern and southern aspects in this zone and has nearly twice as many species on the north slopes as on the south.

V. ZOOGEOGRAPHICAL AFFINITIES

The Coleoptera from the North-West Himalaya (tables XI & XII, fig. 7) are predominantly Palaearctic, especially the Palaearctic of Aisa. The species with undoubted affinities to the Palaearctic of Europe constitute only about 4% of the total. The Oriental element, representing 23%, appears to be comparatively recent instrusions from the plains up the outer ranges and by way of valleys. Although we know so little of the Coleoptera of Tibet, the bulk of the Palaearctic species of the North-West Himalaya extend into Tibet and Central Asia.

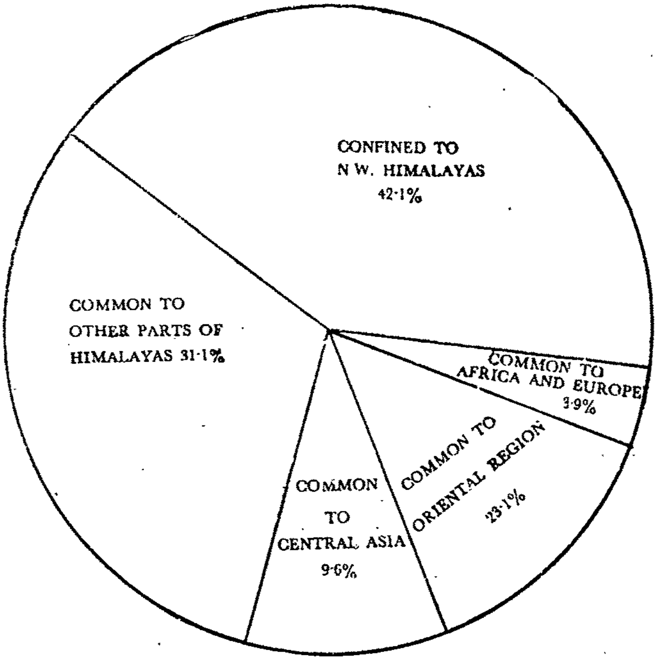

Fig. 7. Zoogeographical composition of Coleoptera from the North-West Himalaya.

About 10% of the species are common to the North-West Himalaya, Central Asia and Tibet. Nearly 31% of them comprise species which also occur in other parts of the Himalaya and often extend as far east as Teesta

Valley. . The species which are found exclusively in North-West Himalaya amount to about 42% of the total. The faunal sampling limits of the different zoogeographical elements contained in table XII show extremely interesting results. In order to come across, for example, at least one species which is common to North-West Himalaya and the Palaerctic of Europe, random collections of as many as 40 species must be made in the region. The maximum frequency of occurrence is not likely to be more than 2 under these conditions. This is a very significant indication of the relative scarcity of the European species.

Several well known Palaearctic genera like *Carabus*, *Calosoma*, *Harpalus*, *Calathus*, *Amara*, *Pterostichus*, *Anchomenus*, *Bembidion*, *Loricera*, *Paropisthius*, *Notiophilus*, *Nebria*, *Leistus*, *Pristonychus*, *Lissopogonus* and *Sphodrus* occur only in the Himalaya in the Indian faunal limits. These also include the genera which are frequently met with in the North-West Himalaya. While most of the genera occurring in the North-West Himalaya have Holarctic allies, *Parepisthius* from the North-West Himalaya is represented by a single species from the Nearctic of North America.

A little more than one half of the whole Carabidae representes species restricted wholly to the region, while one-third of the total species are also found in the Himalaya east of the R. Sutlej. About one-seventh represents species common to the North-West Himalaya and the Palaearctic of Asia north of the Himalaya. The Oriental element in the Carabidae is also about the same. The European element is hardly one-twenth-fifth of the total. *Anchomenus quadripunctatus* occurs in the Himalaya and throughout the Holarctic. *Amara brucei* and *Bembidion nivicola* are found in the North-West Himalaya and the Eastern Himalaya. *Broscus punctatus* Dej.extends throughout the Himalaya, Mt. Sinai, Egypt and Iraq.

The Trechini are on the whole Palaearctic forms. With the exception of the single species, *Perileptus ceylonicus* Nietn., the Trechini from India are confined to the Himalaya. The genus *Lissopogonus* is also not known outside the Himalaya in India. *Chlaenius tenuelimbatus* Ball occurs in the Himalaya and Central Asia. The genus *Omophron* also seems to be equally confined to the Himalaya, though one or two species are known to extend asfar south as Vindhyas.

There seems to be no resemblance between the European and the North-West Himalayan Hydrophilidae, Gyrinidae, Dytisidae, Cicindelidae, Paussidae, Histeridae, Curculionidae and other families.

Species of Gyrinidae, Cicndelidae, Paussidae, Endomychidae, llidae and Meloidae represent more or less deep penetrations from the Oriental realm of India.

The families represented by species common to the North-West Himalaya and the Asian Palaearctic include Carabidae, Hydrophilidae, Cicindelidae, Staphylinidae, Curculionidae and Scarabaeidae. The Species of Nitidulidae, Rhysodidae, Erotelidae and Dynastidae, occurring in the North-West Himalaya have not so far been found in the rest of the Himalaya.

Nearly two-thirds of the Staphylindae from the North-West Himalaya are restricted to the region. Less than half of them are common to the region and the rest of the Himalaya. Species common to the European Palaearctic, other neighbouring regions of the Asiatic table-land and India are extremely few. Taken as a whole the family seems to be represented by species which have evolved since the Pleistocene.

Except one species, the rest of the family Histeridae found in the North-West Himalaya appears to be restricted to the region.

In the family Curculionidae two-thirds of the species are typically North-West Himalayan and a sixth also occurs in the rest of the Himalaya and Tibet and other Asian Palaearctic regions. The Oriental element seems to be exceedingly rare.

The families Scarabaeidae and Rutelidae present interesting features. Only a single species of the former and five of the latter family appear to be restricted, while about 20 species of the family Scarabaeidae found in the North-West Hlimalaya also extend to the east of R. Sutlej. While only 7 of the total Scarabaeidae are found in the Asian Palaearctic, the Oriental element is nearly twice as frequent.

Some species are also common to the Himalayan and the European Palaearctic. In the case of Rutelidae the great bulk of the species, representing almost three-fourths the total number, extend throughout the Himalaya. The Oriental element is weaker than in Scarabaeidae.

The family Cetonidae includes species representative of nearly all the types discussed.

Twenty out of the 43 species of Chrysomelidae are confined to the North-West Himalaya and about the same number is common to the region and the Himalaya east of R. Sutlej There is a fairly considerable Oriental element also.

TABLE I. Percentage distribution and sampling limits of families

Serial No.	Family	Genus		Species		Standard deviation	Sampling limits out of 100	
		Actual No.	Percentage	Actual No.	Percentage			
1.	Cicindelidae	3	1.3	16	2.7	0.540	1	3
2.	Carabidae	62	28.0	212	36.5	1.812	32	36
3.	Dytiscidae	4	1.8	4	0.69	0.810	...	...
4.	Gyrinidae	2	0.9	2	0.34	0.143	...	...
5.	Paussidae	1	0.5	1	0.17	0.129	...	...
6.	Hydrophilidae	4	1.8	5	0.86	0.293	...	...
7.	Histeridae	2	0.9	17	2.90	0.54	1	3
8.	Staphylinidae	40	18.0	119	20.5	1.283	16	20
9.	Lycidae	2	0.9	7	1.2	0.351	0	1
10.	Rhysodidae	1	0.5	1	0.17	0.129	...	...
11.	Nitidulidae	2	0.9	2	0.34	0.143	...	...

(Contd.)

TABLE I. Percentage distribution and sampling limits of families. (*Contd.*)

Serial No.	Family	Genus		Species		Standard deviation	Sampling limits out of 100	
		Actual No.	Percentage	Actual No.	Percentage			
12.	Erotelidae	2	0.9	2	0.34	0.143	...	...
13.	Endomychidae	1	0.5	1	0.17	0.129	...	...
14.	Coccinellidae	4	1.8	4	0.69	0.256	...	...
15.	Meloidae	1	0.5	1	0.17	0.129	...	...
16.	Scarabaeidae	9	3.9	26	4.4	0.206	3	4
17.	Rutelidae	6	2.6	21	3.6	0.189	3	4
18.	Dynastidae	3	1.3	3	0.51	0.235	...	...
19.	Cetonidae	7	3.1	11	1.9	0.137	0	1
20.	Cerambycidae	13	5.8	15	2.5	0.156	2	2
21.	Chrysomelidae	32	14.3	43	7.4	0.261	6	7
22.	Curculionidae	22	9.8	67	11.5	1.012	8	11
	Total	223*		580*				

*Several of species of Tenebrionidae have not been included in this analysis.

The percentages are out of the total Coleoptera from the entire North-West Himalaya.

TABLE II. Percentage distribution of Coleoptera in relation to the aspects of the mountain ranges in North-West Himalaya

No.	Families	Percentage species in the North-West Himalaya as a whole			Percentage species in I Zone		Percentage species in II Zone		Percentage species in III Zone	
		S	N	C	S	N	S	N	S	N
1.	Cicindelidae	81.3	16.7	...	81.2	18.8	...	...	...	...
2.	Carabidae	57.2	26.2	16.6	73.2	26.8	51.4	48.6	37.5	62.5
3.	Dytiscidae	100	...	...	100	...	...	...	...	...
4.	Gyrinidae	100	...	...	100	...	...	...	...	...
5.	Paussidae	100	...	...	100	...	...	...	...	...
6.	Hydrophilidae	71.4	14.3	14.3	100	...	...	100	...	...
7.	Histeridae	88.8	5.6	5.6	100	...	66.7	33.3	...	100
8.	Staphylinidae	35.4	62.2	2.4	38.1	61.9	...	100	...	100
9.	Lycidae	100	...	...	100	...	...	...	...	...
10.	Rhysodidae	100	...	...	100	...	...	...	...	...
11.	Nitidulidae	100	...	...	100	...	...	...	...	...
12.	Erotelidae	50.	50	...	50	50	...	...	...	...
13.	Endomychidae	100	...	...	100	...	...	...	...	...

(Contd.)

TABLE II. Perçentage distribution of Coleoptera in relation to aspects of the mountain rages in North-West Himalaya.—(*Contd.*)

No.	Families	Percentage species in the North-West Himalaya as a whole			Percentage species in I Zone		Percecntage species in II Zone		Percentage species in III Zone	
		S	N	C	S	N	S	N	S	N
14.	Coccinellidae	30	40	30	60	40	33.3	66.7	...	100
15.	Meloidee	50	50	...	50	50	50	50	...	100
16.	Scarabaeidae	66.6	16.7	16.7	80	20	33.3	66.7	...	100
17.	Rutelidae	87.5	8.3	4.2	100	...	...	100	...	...
18.	Dynastidae	100	...	...	100	...	...	...	...	...
19.	Cetonidae	84.6	7.7	7.7	90.9	9.1	...	...	...	...
20.	Cerambycidae	93.3	6.7	...	93.3	6.7	...	...	...	...
21.	Chrysomelidae	89.1	9.7	2.2	100	...	40	60	...	100
22.	Curculionidae	71.3	17.2	11.5	93.7	6.3	31.6	68.4	...	100
	Average	63.5	23.2	13.3	86.8	13.4	30.6	69.3	4.7	95.3

S=Southern slopes, N=Northern slopes, C=Common to southern and northern slopes

Table III. Maximum altitude record of Coleoptera in the Himalaya

Families	Species	Max. altitude in feet in the N. W. H.	Max. altitude in other parts of Himalaya	
CARABIDAE	Amara brucei	17,400	16,500	Mt. Everest Base Camp.
CICINDELIDAE	Cicindela sublacerata balucha	11,000	—	
PAUSSIDAE	Platyrhopalus angustus major	5,500		
	Pausus nauceras		7,000	Mussurie
RHYSODIDAE				
STAPHYLINIDAE	Atheta (Oreostibia) nimbicola	13,000		
	Atheta (Bessobia) submetallica	15,935		
	Atheta (Microdota) ladakiana	15,985		
	Atheta (Paraloconota) dissociata	—	15,750	N. Kumaon
	Atheta (Microdota) scabriventris	—	15,000	Sapi River (Tibet)
	Atheta (Metaxya) nimborum	—	14,500	Sangcha (N. Kumaon)
	Atheta (Dimetrota) altivagans	—	14,500	Sangcha (N. Kamaon)
	Geodromicus brevitarsus	—	15,750	Shelsheel (N. Kamaon)
HISTERIDAE	Hister (4 species)	10—11,000	—	
CURCULIONIDAE	Achlaenomus (2)	11—12,000		
	Blosyrodes (2)	11—12,000		
	Calomycterus (1)	11—12,000		
	Catopionus (1)	11—12,000		
	Heteronyx (2)	11—12,000		
	Lagenolobus (1)	11—12,000		
	Leptomias (2)	11—12,000		
	Myllocerus (1)	11—12,000		
	Rhyncolus (1)	11—12,000		

(*Contd.*)

TABLE III. Maximum altitude record of Coleoptera in the Himalaya (*Contd.*)

Families	Species	Max. altitude in feet in the N. W. H.	Max. altitude in other parts of Himalaya	
	Scepticus (1)	11—12,000		
	Sitones (2)	11—12,000		
	Xylinophorus (1)	11—12,000		
	Catapionus semivittatus	—	15—16,000	Teesta valley (Sikkim)
	Achlaenomus montarum	—	13—14,400	Teesta valley (Sikkim)
	Leptomias waltoni	—	13,000	Gyangtse (Tibet)
EROTYLIDAE	Tetratritoma angusta	9,900		
	Tetratritoma militaris	—	10,000	Nepal—Sikkim Frontier
	Dactylotritoma apicata	—	8—11,000	Pindar valley (U. P.)
ENDOMYCHIDAE	Mycetina montivaga	7,000		
	Stenotarsus seminalis	—	9,000	Garhwal
SCARABAEIDAE	Onthophagus concolor	11,000		
	Onthophagus tibitanus	10,000	13,000	Tibet
RUTELIDAE	Callistopopilia iris	10—11,000	13,000	Tibet
DYNASTIDAE	Alissonotum binodulum	7,000		
CETONIDAE	Rhomborrhina glaberrima	7—8,000	7,000	Mussurie
CERAMBYCIDAE	Leptura rubriola	11,000		
	Purpuricenus montanus	—	13,000	Tibet
CHRYSOMELIDAE	Leptosonyx octocostatus	15,000		
	Swargia nila	—	16,500	Tibet: Karoba Pass

TABLE IV. Analysis of families in the three altitudinal zones

Serial No.	Family	First Zone		Second Zonae		Third Zone	
		Family index	Zonal index	Family index	Zonal index	Family index	Zonal index
1.	Cicindelidae	100	3.00	...	...	...	...
2.	Carabidae	88.68	35.00	37.73	60.60	5.18	50.0
3.	Dytiscidae	100	0.74	...	...	...	...
4.	Gyrinidae	100	0.37	...	...	...	...
5.	Paussidae	100	0.19	...	...	...	...
6.	Hydrophilidae	80	0.74	40.00	1.51	20.0	4.5
7.	Histeridae	88.23	2.78	23.50	3.03	...	...
8.	Staphylinidae	96.63	21.13	8.30	7.57	2.5	13.4
9.	Lycidae	100	1.3	...	...	...	...
10.	Rhysodidae	100	0.19	...	...	...	...
11.	Nitidulidae	100	0.37	...	...	...	...
12.	Erotylidae	100	0.37	...	...	...	...
13.	Endomychidae	100	0.19	...	...	...	...
14.	Coccinellidae	100	0.74	50.00	1.51	50.0	9.0
15.	Meloidae	100	0.19	100.00	0.75	...	...
16.	Scarabaeidae	100	4.83	11.50	2.27	3.8	4.5
17.	Rutelidae	100	3.90	14.20	2.27	...	...
18.	Dynastidae	100	0.56	...	...	...	...
19.	Cetonidae	100	2.04	...	...	...	...
20.	Cerambycidae	93.33	2.60	26.60	3.03	13.3	9.0
21.	Chrysomelidae	97.60	7.80	9.30	3.03	2.3	4.5
22.	Curculionidae	88.00	10.90	26.80	13.60	19.4	4.5
	Zonal total	538		132		22	
	Average Family index	97.4		26.8		14.3	
	Average Zonal index		4.6		7.7		12.5

TABLE V. Altitudinal succession of Genera in Carabidae in the North-West Himalaya at intervals of 2,000 ft.

The numbers in brackets indicate the number of species in each case.

Serial No.	6000-8000	8000-10,000	10,000-12,000	12,000-14,000	Over 14,000
1.	Bembidion (35)	Bembidion (22)	Bembidion (22)	Bembidion (8)	Bembidion (8)
2.	Calosoma (5)	Calosoma (4)	Calosoma (4)	Calosoma (1)	...
3.	Abacetus (2)	Abacetus (1)	Abacetus (1)	...	...
4.	Amara (7)	Amara (6)	Amara (6)	Amara (1)	Amara (1)
5.	Anchomenus (7)	Anchomenus (5)	Anchomenus (6)	...	...
6.	Asaphidion (3)	Asaphidion (1)	Asaphidion (1)	...	...
7.	Bradytus (1)	Bradytus (1)	Bradytus (1)	...	...
8.	Broscus (1)	Broscus (1)	Broscus (1)	...	...
9.	Calathus (3)	Calathus (2)	Calathus (2)	...	...
10.	Callistomimus (1)	Callistomimus (1)	Callistomimus (1)	...	...
11.	Carabus (12)	Carabus (8)	Carabus (1)	...	...
12.	Chlaenius (10)	Chlaenius (1)	Chlaenius (2)	...	...
13.	Chydaeus (1)	Chydaeus (1)	Chydaeus (1)	...	...
14.	Harpalus (4)	Harpalus (5)	Harpalus (4)	...	...
15.	Mastax (2)	Mastax (1)	Mastax (2)	...	...

(*Contd.*)

TABLE V. Altitudinal succession of Genera in Carabidae in the North-West Himalaya at intervals of 2,000 ft. The numbers in brackets indicate the number of species in each case.—(*Contd.*)

Serial No.	6000-8000	8000-10,000	10,000-12,000	12,000-14,000	Over 14,000
16.	Metabletus (2)	Metabletus (1)	Metabletus (1)	...	...
17.	Nebria (2)	Nebria (6)	Nebria (3)	...	...
18.	Pardileus (2)	Pardileus (2)	Pardileus (1)	...	...
19.	Phaeropsophus (2)	Phaeropsophus (2)	Phaeropsophus (2)	...	...
20.	Pristonychus (3)	Pristonychus (2)	Pristonychus (2)	...	...
21.	Scarites (5)	Scarites (2)	Scarites (1)	...	...
22.	Stenolophus (3)	Stenolophus (1)	Stenolophus (1)	...	...
23.	Trechus (3)	Trechus (4)	Trechus (2)	...	...
24.	Amolops (1)	Amolops (2)	Amolops (1)	...	...
25.	Clivinia (1)	Clivinia (1)	Clivinia (1)	...	...
26.	...	Hypsinephus (1)	Hypsinephus (1)	...	...
27.	...	Liocnemis (1)	Liocnemis (1)	...	...
28.	...	Trichocellus (1)	Trichocellus (1)	...	...
29.	...	...	Chaetobroscus (1)	...	...
30.	...	...	Cymindis (3)	...	

(*Contd.*)

TABLE V. Altitudinal succession of Genera in Carabidae in the North-West Himalaya at intervals of 2,000 ft. The numbers in brackets indicate the number of species in each case.—(*Contd.*)

Serial No.	6000-8000	8000-10,000	10,000-12,000	12,000-14,000	Over 14,000
31.	...	...	Drypta (1)	...	...
32.	...	...	Dyschirius (1)	...	...
33.	...	...	Licinus (1)	...	...
34.	Acinopus (2)	Acinopus (3)	...	...	...
35.	...	Leistus (1)	...	...	...
36.	Axonya (1)	...	...	...	...
37.	Brachinus (4)	...	...	...	...
38.	Coelostomus (1)	...	...	...	...
39.	Craspedonotus (1)	...	...	...	...
40.	Cyclosomus (1)	...	...	...	...
41.	Kareya (1)	...	...	...	...
42.	Notiophilius (1)	...	...	...	...
43.	Omophron (2)	...	...	...	...
44.	Platymetopius (1)	...	...	...	...
45.	Sphodrus (1)	...	...	...	...
46.	Tachys (5)	...	...	...	...

(*Contd.*)

TABLE V. Altitudinal succession of Genera in Carabidae in the North-West Himalaya at intervals of 2,000 ft. The numbers in brackets indicate the number of species in each case.—(*Contd.*)

Serial No.	6000-8000	8000-10,000	10,000-12,000	12,000-14000	Over 14,000
47.	Tetragonoderus (1)	...	...	...	...
48.	Orthotrichus (1)	...	...	...	...
49.	Acupalpus (1)	...	...	...	...
50.	Anthia (1)	...	...	...	...
51.	Apristus (1)	...	...	...	...
52.	Coleolissus (1)	...	...	...	...
53.	Colpodes (3)	...	...	...	...
54.	Cymindoides (1)	...	...	...	...
55.	Diplocheila (1)	...	...	...	...
56.	Dromius (1)	...	...	...	
57.	Euleptus (1)	...	...	...	...
58.	Ophonus (2)	...	...	...	...
59.	Orthogonius (1)	...	...	...	...
60.	Pterostichus (1)	...	...	...	...
61.	Rhopalopalpus (1)	...	...	...	...
62.	Stephana (1)	...	...	...	...

TABLE VI. Altitudinal Species succession in *Bembidion* (Carabidae) in the North-West Himalaya at intervals of 2,000 ft.—

Serial No.	6,000–8,000	8,000–10,000	10,000–12,000	12,000–14,000	Above 14,000
1.	bracculatum	bracculatum	bracculatum	bracculatum	bracculatum
2.	fuscicrus	fuscicrus	fuscicrus	fuscicrus	fuscicrus
3.	irregularae	irregularae	irregularae	irregularae	irregularae
4.	...	pluto	pluto	pluto	pluto
5.	...	...	bucephalum	bucephalum	bucephalum
6.	...	...	...	nivicola	nivicola
7.	...	...	...	petrimagnai	petrimagnai
8.	...	...	...	...	hutchinsoni
9.	hasurada	hasurada	hasurada	hasurada	...
10.	luntaka	luntaka	luntaka	luntaka	...
11.	algidum	algidum	algidum	...	...
12.	betegara	betegara	betegara	...	...
13.	exaratum	exaratum	exaratum	...	...
14.	himalayanum	himalayanum	himalayanum	...	...
15.	orinum	orinum	orinum	...	...

(*Contd.*)

TABLE VI. Altitudinal Species succession in *Bembidion* (Carabidae) in the North-West Himalaya at intervals of 2,000 ft.

Serial No.	6,000–8,000	8,000–10,000	10,000–12,000	12,000–14,000	Above 14,000
16.	satanas	satanas	satanas	...	...
17.	...	aquilum	aquilum	...	...
18.	...	gagates	gagates	...	...
19.	...	livens	livens	...	...
20.	...	...	ajmonis	...	...
21.	...	...	ladakenese	...	...
22.	...	...	ladas	...	...
23.	...	...	leve	...	...
24.	...	...	pamiricola	...	...
25.	...	...	beesoni	...	...
26.	babaulti	babaulti	...	...	...
27.	caporiaccoi	caporiaccoi	...	...	...
28.	psilodorum	psilodorum	...	...	...
29.	dardum	dardum	...	...	...
30.	...	atlanta	...	...	...

(*Contd.*)

TABLE VI. Altitudinal Species succession in *Bembidion* (Carabidae) in the North-West Himalaya at intervals of 2,000 ft.

Serial No.	6,000–8,000	8,000–10,000	10,000–12,000	12,000–14,000	Above 14,000
31.	...	ixion	...	...	...
32.	...	manicatum	...	...	...
33.	cameroni	...	...	...	...
34.	clops	...	...	...	...
35.	dux	...	...	...	...
36.	eupages	...	...	...	...
37.	eutherum	...	...	...	...
38.	gilgiti	...	...	...	...
39.	holoconotum	...	...	...	...
40.	kashmirense	...	...	...	...
41.	limatum	...	...	...	...
42.	lissonotum	...	...	...	...
43.	ochropus	...	...	...	...
44.	regale	...	...	...	...
45.	rubidum	...	...	...	...

(Contd.)

TABLE VI. Altitudinal Species succession in *Bembidion* (Carabidae) in the North-West Himalaya at intervals of 2,000 ft.—(*Contd.*)

Serial No.	6,000–8,000	8,000–10,000	10,000–12,000	12,000–14,000	Above 14,000
46.	sillemi	...	...	...	...
47.	surdum	...	...	...	...
48.	uvidum	...	...	...	...
49.	varium	...	...	...	...
50.	xestum	...	...	...	...
51.	trimaculatum	...	...	...	...
52.	discordens	...	...	...	...

TABLE VII. Analysis of the overlapping of the ranges of altitudinal distribution of Coleoptera

S. No.	Component element	*First Zone* Percent.	*Second Zone* Percent.	*Third Zone* Percent.
1.	Species confined to the zone.	80	23	17
2.	Species occurring in the first zone also.	...	66	39
3.	Species occurring in the second zone also.	17	...	44
4.	Species occurring in the third zone also.	3	11	...

TABLE VIII. Analysis of the overlapping of ranges of altitudinal distribution of Carabidae

Serial No.	Component element	*First Zone* Percent.	*Second Zone* Percent.	*Third Zone* Percent.
1.	Species confined to the zone.	67	24	18
2.	Species occurring in the first zone also.	...	67	35
3.	Species occurring in the second zone also.	30	...	47
4.	Species occurring in the third zone also.	3	9	...

TABLE IX. Zonal percentage distribution and sampling limits for total Coleoptera

Serial No.	Zones	Percentage of species	Standard deviation	Sampling limits									
				10		20		30		40		50	
1.	First Zone	78	1.308	3	10	11	20	19	27	27	35	35	43
2.	Second Zone	19	1.237	0	6	0	8	2	9	4	11	5	13
3.	Third Zone	3	1.540	0	2	0	2	0	3	0	3	0	3

Percentage out of the total number of the three zones combined

TABLE X. Zonal percentage distribution and sampling limits for Carabidae

Serial No.	Zones	Percentage of species	Standard deviation	Sampling limits									
				10		20		30		40		50	
1.	First Zone	67	1.485	2	10	9	15	15	25	25	31	29	38
2.	Second Zone	29	1.429	0	7	1	10	4	13	7	16	10	19
3.	Third Zone	4	0.196	0	1	0	2	0	2	1	2	1	3

TABLE XI. Zoogeographical analysis of families

Serial No.	Family	Species confined to N.W.H	Species common to other parts of Himalaya	Species common to Central Asia	Species common to Oriental of India	Species common to Africa & Europe
1.	Cicindelidae	0	11	4	8	1
2.	Carabidae	117	77	29	30	9
3.	Dytiscidae	2	2	...	...	...
4.	Gyrinidae	...	1	...	1	1
5.	Paussidae	...	1	...	1	...
6.	Hydrophilidae	1	1	...	1	1
7.	Histeridae	16	1	...	...	...
8.	Satphylinidae	70	46	2	1	4
9.	Lycidae	3	4	1	2	...
10.	Rhysodidae	1	...	...	...	...
11.	Nitidulidae	1	...	...	1	...
12.	Erotylidae	1	...	1	...	...
13.	Endomychidae	...	1	...	...	...
14.	Coccinellidae	...	4	4	4	4
15.	Meloidae	...	1	...	1	...
16.	Scarabaeidae	1	19	7	14	5
17.	Rutelidae	5	15	3	5	...
18.	Dynastidae	1	...	1	1	1
19.	Cetonidae	4	4	2	4	1
20.	Cerambycidae	8	4	4	4	...
21.	Chrysomlidae	20	19	3	8	2
22.	Curculionidae	49	11	11	5	...
	Total	300	222	69	93	28

TABLE XII. Analysis and Sampling limits of the Zoogeographical composition of total Coleoptera

Serial No.	Zoogeographical elements.	Actual No. of sp.	%	p.	q.	Standard deviation	Limits of Sampling							
							10		20		30		40	
1.	North-West Himalayan	300	42.1	0.421	0.579	1.559	0	9	4	15	7	18	12	21
2.	Other Himalayan	222	31.1	0.311	0.689	1.466	0	8	1	11	4	14	8	17
3.	Asian Palaearctic	69	9.6	0.096	0.914	0.295	1	2	1	3	1	4	2	5
4,	Oriental	93	23.1	0.231	0.769	1.328	0	7	0	9	2	11	5	14
5.	European Palaearctic	28	3.9	0.039	0·961	0.061	0	1	0	1	0	2	1	2
	Total	712												